Propylene / 1-pentene random copolymers: preparation, characterisation and commercialisation

by

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DECLARATION

I, the undersigned hereby declare that the work contained in this thesis is my own original work and has not previously, in its entirety or in part, been submitted at any University for a degree.

ABSTRACT

Most polypropylene copolymers commercially available have ethylene, and to a lesser degree 1-butene as comonomers. Commercially available higher α-olefins, mostly even-numbered, are seldom used for the production of PP copolymers, probably due to cost. Sasol's Fischer-Tropsch oil-from-coal process produces many linear and branched α-olefins as by-products that can be isolated and purified by a relatively cheap refinery process, including the odd-numbered 1-pentene olefin. Sasol's gas-phase Novolen PP plant at Secunda, South Africa is ideally suited to the manufacture of high quality PP random copolymers. As such an opportunity was identified to research the use of higher α-olefins, and more specifically 1-pentene, in the gas-phase production of PP random copolymers.

Different methods to produce propylene / 1-pentene random copolymers in the slurry phase on bench-scale were investigated. A procedure was subsequently developed to produce propylene / 1-pentene random copolymers in the gas-phase in 10 litre autoclaves. It was found that commercially available fourth generation supported catalysts successfully incorporated the bulky 1-pentene monomer into the propylene backbone, both during slurry and gas-phase polymerisations. Software modelling was employed to determine the dew points of selected gas mixtures typically found during the production of PP random copolymers. The results indicated that typical process conditions could be employed during the gas-phase polymerisation of propylene and 1-pentene without the risk of condensation taking place inside the reactor.

Propylene / 1-pentene random copolymers were subsequently successfully produced on the 800 litre BASF pilot plant in Germany followed by the first commercial production of the copolymer on Sasol's 50m^3 Novolen gas-phase plant at Secunda. Using commercially available software the impact of introducing 1-pentene as comonomer during the production of random copolymers on the condenser cooling capacity was evaluated. Feasible and safe plant operating conditions were established for the production of propylene / 1-pentene random copolymers.

The relationship between operating pressure and powder morphology was investigated to optimise process conditions. Operating at higher pressure in the gas-phase increases the monomer concentration in the reactor and as such improves the space/time/yield ratio of the 50m^3 reactors. It was shown that higher operating pressures could be employed through the introduction of 1-pentene as comonomer during the production of PP random copolymer.

The dramatic increase in catalyst productivity observed during the 800 litre pilot plant trials, up to a comonomer ratio of about 5%, supported the results obtained from a kinetic study carried out in bench-scale autoclaves.

A comprehensive study was undertaken to compare the rheological, thermal, crystallisation, physical and mechanical properties of propylene / 1-pentene random copolymers with those of commercially available PP random copolymers. A series of propylene homo- and random copolymers with 1-pentene and ethylene as comonomers respectively, was prepared. NMR and IR techniques were developed to facilitate the determination of copolymer composition for the new family of 1-pentene random copolymers.

The effect of comonomer content, molecular weight and temperature on the properties of the series of polymers was investigated. The propylene / 1-pentene random copolymers show unique rheological behaviour associated with the short propyl branches in the polymer backbone with minimum zero shear viscosity at about 2% 1-pentene content. The effect of molecular structure changes with comonomer content were analysed by the calculation of square average end-to-end distance, packing length, tube diameter, molecular mass between entanglements and critical molecular mass. The viscosity of the 1-pentene random copolymers shows higher shear and temperature sensitivity compared to propylene homo- and ethylene random copolymers.

The thermodynamic melting point of the propylene / 1-pentene random copolymers showed a significant decrease with increasing comonomer content in the 0 to 5% range. A wider melting range and higher peak melting point depression rate was observed compared to ethylene random copolymers at similar and increasing comonomer content measured on a weight % basis. It was found that the crystal structure of the propylene / 1-pentene random copolymers contains both the α- and the γ-modifications with the ratio of the respective crystal forms a function of both comonomer content and crystallisation temperature. The glass temperature decreased slightly with increasing comonomer (1-pentene) content.

It is proposed that the short branch (propyl) “defects” in the polymer backbone are incorporated into the crystal lattice resulting in increased rate of melting point depression with increasing (wt%) comonomer content compared to other random copolymers while maintaining relative high stiffness. The propylene / 1-pentene random copolymers exhibit the lowest haze values compared to all commercially available PP random copolymers at corresponding levels of comonomer content on a wt% basis. The stiffness to haze ratio of propylene / 1-pentene random copolymers are unique for all the members of the PP family. An inverse relationship between comonomer content and the measured tensile yield strength and modulus is observed.

Application studies conducted on the propylene / 1-pentene random copolymers highlighted several interesting characteristics. Films produced from these copolymers exhibited very low haze and xylene soluble values while maintaining mechanical integrity. In the BOPP application the combination of processability and premium film properties presents a unique opportunity for the family of propylene / 1-pentene random copolymers.

Blow moulding and injection moulding trials highlighted several advantages of product properties manufactured with propylene / 1-pentene random copolymers if compared to other commercially available random copolymers. The 1-pentene randoms presented lower in-mould as well as total shrinkage than ethylene based random copolymers.

Stabilisation and nucleation studies conducted on the propylene / 1-pentene random copolymers showed that a typical combination antioxidant package and nucleating agent, at normal loading levels, could be used.

In the larger PP random copolymer family 1-pentene imparts a better balance of properties than other comonomers. The combination of low melting point and xylene solubles with high stiffness and clarity is unique to propylene / 1-pentene random copolymers.

OPSOMMING

Die oorgrote meerderheid van kommersieel beskikbare polipropileen (PP) kopolimere het etileen, en tot 'n mindere mate buteen, as komonomeer. Die relatief hoë koste van kommersieel beskikbare hoër alfa-olefiene is moontlik die rede waarom hulle selde gebruik word vir die vervaardiging van PP kopolimere. Die Sasol Fischer-Tropsch proses, waartydens olie uit steenkool vervaardig word, lewer verskeie liniêre en vertakte alfa-olefiene as neweprodukte wat geïsoleer en gesuiwer kan word in 'n relatiewe goedkoop rafineringsproses. Dit sluit ook die onewe-koolstofgetal 1-penteen-olefien in. Sasol se gasfase Novolen PP aanleg in Secunda, Suid-Afrika, is besonder geskik vir die vervaardiging van hoë standaard PP statistiese kopolimere. Voortvloeiend hieruit is die geleentheid geidentifiseer om die gebruik van hoër alfa-olefiene, en meer spesifiek 1-penteen, na te vors tydens die gasfase-produksie van PP statistiese kopolimere.

Verskeie metodes om propeleen / 1-penteen statistiese kopolimere in 'n koolwaterstofoplosmiddel op laboratoriumskaal te produseer, is ondersoek. 'n Prosedure is daarna ontwikkel om propileen / 1-penteen statistiese kopolimere ook in die gasfase te vervaardig in 10-liter drukvate. Die bevinding was dat kommersieel beskikbare vierde-generasie ondersteunde kataliste die swaarder 1-penteenmonomeer suksesvol geïnkorporeer het in die propileenketting tydens beide die koolwaterstof oplosmiddel- en gasfase polimerisasiereaksies. Rekenaargebaseerde modellering is gebruik om die kondensasiekondisies van tipiese gasmengsels, teenwoordig tydens die produksie van PP statistiese kopolimere, te bepaal. Die resultate het aangedui dat normale proseskondisies tydens die gasfasepolimerisasie van propileen en 1-penteen geen risiko van kondensasie in die reaktor inhou nie.

Propileen / 1-penteen statistiese kopolimere is gevolglik met groot sukses vervaardig by die 800-liter BASF loodsaanleg in Duitsland, gevolg deur die eerste kommersiële vervaardiging van die kopolimeer op die Sasol 50m^3 Novolen gasfase-aanleg in Secunda. Deur gebruik te maak van kommersieel beskikbare sagteware, is die impak van 1-penteen as komonomeer tydens die vervaardiging van statistiese kopolimere op die verkoelingskapasiteit van die kondensator bepaal. Veilige en uitvoerbare aanlegkondisies is uitgestip vir die vervaardiging van propileen / 1-penteen statistiese kopolimere.

Die verhouding tussen die reaktordruk en poeiermorfologie is ondersoek om die prosestoestande te optimiseer. Vervaardiging van kopolimere in die gasfase by hoër drukke lei tot verhoogde monomeerkonsentrasie in die reaktor en gevolglik hoër produksiedeursette. Daar is bewys dat tydens die produksie van PP statistiese kopolimere, met 1-penteen as komonomeer, hoër reaktordruk ingespan kan word.

Die dramatiese toename in katalisproduktiwiteit waargeneem tydens die 800-liter loodsaanleg proefloop, tot en met 'n komonomeer inhoud van ongeveer

5%, word ondersteun deur die resultate van 'n kinetiese studie uitgevoer in laboriumskaal drukvate.

'n Omvattende studie, om die reologiese, termiese, kristallyne, fisiese en meganiese eienskappe van propileen / 1-penteen statistiese kopolimere te vergelyk met kommersieel beskikbare PP statistiese kopolimere, is uitgevoer. 'n Reeks propileen homo- en statistiese kopolimere, met 1-penteen en etileen as komonomere onderskeidelik, is berei. KMR- en IR- tegnieke is ontwikkel om die bepaling van komonomeersamestelling vir die nuwe familie van 1-penteen statistiese kopolimere te fasiliteer.

Die invloed van komonomeersamestelling, molekulere gewig en temperatuur op die eienskappe van die reeks polimere is ondersoek. Die propoleen / 1-penteen statistiese kopolimere toon unieke reologiese eienskappe wat geassosieer kan word met die propielsykettings in die polimeerruggraat. Die viskositeit van die propileen / 1-penteen statistiese kopolimere toon 'n hoër wrywings- en temperatuursensitiwiteit in vergelyking met propileen homo- en etileen statistiese kopolimere.

'n Drastiese verlaging in die termodinamiese smeltpunt van die propileen / 1-penteen statistiese kopolimere met 'n toename in komonomeerinhoud is waargeneem tot en met 'n 5% komonomeerinhoud. Die propileen / 1-penteen statistiese kopolimere toon 'n breër smeltgebied en 'n hoër tempo in die piek smeltpuntafname in vergelyking met etileen statistiese kopolimere met soortgelyke komonomeer inhoud, gemeet op 'n massabasis. Daar is bewys dat die kristalstruktuur van die propileen / 1-penteen statistiese kopolimere beide die alfa en gamma modifikasies bevat. Die verhouding van die onderskeie kristalvorms is 'n funksie van komonomeerinhoud en kristalisasie-temperatuur. 'n Afname in die glastemperatuur met verhoogde komonomeer inhoud is waargeneem.

Die aanname dat die kort propielsykettings in die polimeerruggraat in die kristalstruktuur geïnkorporeer word, is gemaak. Dit verklaar die hoë afname in die tempo van die smeltpunt met toenemende komonomeer inhoud relatief tot ander statistiese kopolimere, met die handhawing van hoë modulus-waardes. Die besondere deursigtigheid van die propileen / 1-penteen statistiese kopolimere tesame met relatief hoë modulus waardes is uniek. 'n Omgekeerde verhouding tussen komonomeer inhoud en treksterkte asook moduluswaardes is waargeneem.

'n Toepassingstudie uitgevoer met die propileen / 1-penteen statistiese kopolimere het verskeie interessante resultate gelewer. Films vervaardig van hierdie kopolimere toon besonderse deursigtigheid en lae waarde van xileen-oplosbaarheid, terwyl meganiese integriteit gehandhaaf word. Voordele in die vervaardigingsproses van BOPP-films asook bogemiddelde filmeienskappe hou unieke moontlikhede vir propileen / 1-penteen statistiese kopolimere in.

Verskeie voordele tydens blaas- en spuitvormingsprosesse is waargeneem relatief tot ander beskikbare statistiese kopolimere. Die 1-penteen statistiese kopolimere toon 'n laer in-vorm sowel as totale krimping relatief tot etileen-

gebaseerde kopolimere. 'n Studie het aangetoon dat tipiese bymiddelpakette by normale toevoegingsvlakke geskik is vir propileen / 1-penteen statistiese kopolimere.

Gesien in die groter PP statistiese kopolimeer familie toon 1-penteen 'n beter balans van eienskappe as ander komonomere. Die kombinasie van laer smeltpunt en xileen-oplosbares met hoë moduluswaardes en helderheid is uniek aan propileen / 1-penteen statistiese kopolimere.

To Anne-Marié and Lienkie
for their contribution to a true love story

and

In memory of my parents

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CHAPTER 1

INTRODUCTION AND OBJECTIVES

This investigation forms part of a research project to develop polypropylene copolymers containing higher alpha olefin co-monomers, especially in the range C5 to C10. More specifically it contributes to the knowledge of producing propylene and 1-pentene random copolymers on a commercial gas-phase plant and the properties of the materials.

1.1 INTRODUCTION

More than 45 years have elapsed since the discovery of the stereo-specific polymerisation of polypropylene by Natta and his co-workers in 1955 [1]. This discovery of a new crystalline polymer heralded a new era in polymer science and technology and, in the years following its discovery, polypropylene went through a dynamic industrial-development cycle.

The world market for polypropylene has grown from 1,5 million tons per annum in 1970 to 13,0 million tons per annum in 1990, and reached 29 million tons per annum at the turn of the century [2, 3]. It is expected that the volume of polypropylene may soon reach the 30 million tons per annum milestone [3]. This exponential growth in the polypropylene market can mostly be attributed to the continuous development of manufacturing processes and focussed research into improved catalytic systems for the production of this extremely versatile polymer. The role of co-monomers in maintaining these high growth rates is, however, not always acknowledged.

There are three main types of polypropylene (PP) available, namely: homopolymers, random copolymers and block copolymers.

In homopolymers, it is exclusively propylene units that form the polymer chain. Isotactic propylene homopolymer, with its high melting point (166°C), is an extremely versatile material. It finds application in many areas, such as: fibres, films, pipes, non-wovens, tapes, thermoformed and blow moulded containers, and wide variety of injection moulded items. However, PP homopolymers are brittle below their glass transition temperature, around 0°C, and exhibit poor transparency.

PP impact (block) copolymers are produced through a sequential polymerisation process, utilising two or more reactors in series. A propylene homopolymer is produced in the first reactor. The reactor powder is then transferred to the second reactor, where a mixture of ethylene and propylene is copolymerised with the same catalyst system. A heterophasic system, consisting of a semi-crystalline matrix with a nearly amorphous elastomeric component dispersed within it, is thus formed. PP impact copolymers show improved low-temperature

impact strength in combination with the retention of stiffness and melting point.

Commercial PP random copolymers are produced by the copolymerisation of propylene with small amounts of (mostly) ethylene or 1-butene [4]. Random PP copolymers have improved transparency and gloss, are tougher, more flexible and softer, and have lower welding and heat sealing temperatures than high crystalline PP homopolymers.

Sasol [5] has a high availability of alpha olefins, especially hexene-1 and pentene-1. Such a study, as this one, of their copolymerisation with propylene can be of benefit in the development of novel random copolymers with unique properties. From a literature study investigating 256 publications in the field of PP copolymers, only 18 referred to propylene / hexene-1 copolymers, and only 2 to propylene / pentene-1 copolymers. These two publications are irrelevant to the present investigation as pentene-1 as copolymer is only very briefly mentioned.

1.2 OBJECTIVES

The Sasol oil-from-coal conversion process, based on the high-temperature Fischer-Tropsch reaction, yields a broad spectrum of hydrocarbons in the C1 – C20 range [5]. This unique process gives Sasol a significant cost advantage over its competitors as high value by-products are produced simultaneously with synthetic oil, as shown in Figure 1.1.

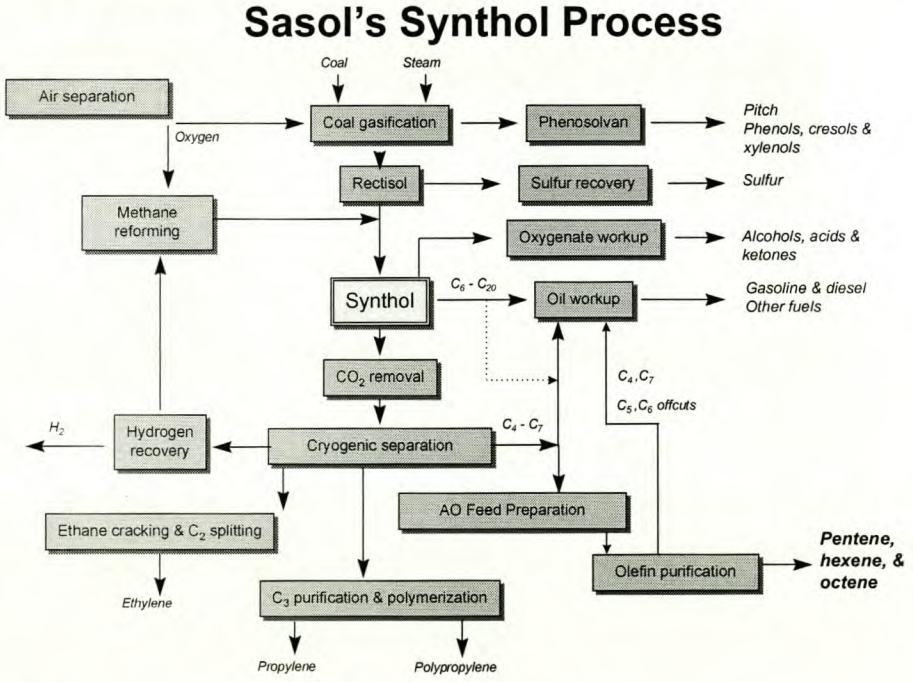

Figure 1.1: Products produced by Sasol's Synthol process

The chemical components include a range of alpha olefins and other olefins, which are separated and purified by a distillation process. The range and volumes of olefins available, as well as the current production capacities, are shown in Figure 1.2.

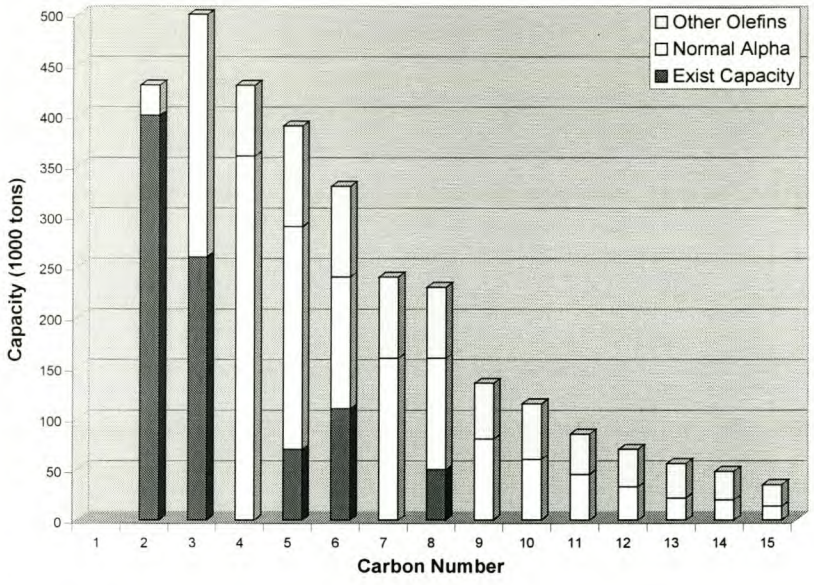

Figure 1.2: Available Alpha Olefin Capacity

Sasol Polymers, a Division of Sasol Chemical Industries, is a world-class producer and supplier of monomers, polymers, chemicals and mining reagents to international markets [6]. An opportunity was identified to selectively research the use of higher alpha olefins in the production of random polypropylene copolymers. Although random polypropylene copolymers represent less than 10% of the total world polypropylene consumption, it is the one area where increased market focus is expected. In many cases PP random copolymers are an interesting alternative to transparent materials such as PVC, polystyrene and glass [7].

Most commercially available propylene copolymers have ethylene as the comonomer, although some do contain 1-butene [8,9]. There are also a number of terpolymers containing both ethylene and 1-butene [9].

The objectives of this study were the following.

- Develop bench-scale slurry, bulk and gas-phase polymerisation techniques that produce PP polymers with similar properties to the PP produced commercially.

- Develop the relevant analytical techniques to enable molecular and macroscopic characterisation of propylene / higher alpha-olefin random copolymers.
- Determine whether commercially produced Ziegler-Natta catalyst systems will incorporate sufficient amounts of 1-pentene and 1-hexene comonomers effectively into the PP polymer backbone. (To be able to incorporate the bulkier 1-pentene and 1-hexene comonomers, the catalyst sites should be "open" enough to allow insertion into the polymer backbone.)
- Compare the rheological, thermal, physical and mechanical properties of propylene / 1-pentene random copolymers with those of commercially available PP random copolymers.
- Determine the feasibility of producing propylene / 1-pentene random copolymers on a commercial gas-phase plant.
- Determine general processing characteristics for commercially available reactors.

1.3 SCOPE

To meet the objectives of this research project, a number of tasks were undertaken, as given below.

1.3.1 Polymerisation at ambient conditions

During this phase, the bench-scale synthesis of PP homo- and random copolymers was explored, using second-generation Ziegler-Natta catalysts under ambient conditions. The properties of the polymers synthesised were compared to those of commercially produced polymer. The drift in comonomer concentrations was studied during the synthesis of the PP random copolymers.

1.3.2 Polymerisation in slurry in a pressure vessel

The huge drift in comonomer concentration during ambient synthesis and lack of effective control of the Melt Flow Index (MFI) highlighted the need for a more controlled reaction environment for the continuation of the project. The effective incorporation of the bulkier 1-pentene and 1-hexene into the polymer backbone, using second-generation Ziegler-Natta catalyst systems, was studied by comparing the copolymer composition with the crystalline structure, using the following techniques:

- Differential Scanning Calorimetry
- Wide Angle X-ray Diffraction
- Light Microscopy.

1.3.3 Gas-phase polymerisation in a pressure vessel

Propylene / 1-pentene random copolymers were prepared in gas-phase, controlling the partial pressures of monomers in the reaction

vessel. The dew points of selected (typical) gas compositions were calculated with available software to determine operating ranges. During this phase of the project third-generation $MgCl_2$-supported Ziegler-Natta catalyst systems were used for the first time. The random copolymers were analysed with regard to their composition and crystalline structure.

1.3.4 Property evaluation

To facilitate an in-depth comparative study into the properties of propylene / 1-pentene random copolymers, a controlled set of polymers was produced. It consisted of propylene homopolymers and random copolymers with ethylene and 1-pentene respectively. This control set of polymers was characterised with regard to composition and molecular weight and distribution.

This comprehensive study of the properties of propylene random copolymers with different 1-pentene contents and viscosities, in relation to commercially available propylene / ethylene copolymers, included:

- Investigation of rheological properties, including: steady state and dynamic shear viscosity, creep compliance and plateau modulus,
- Study of thermal characteristics, including: melting temperature, heat of fusion and glass transition temperatures,
- Determination of crystallisation properties, such as: degree of crystallisation, modifications and kinetics of crystallisation,
- Characterisation of mechanical properties, including: tensile strength, yield strength, elongation, tensile modulus and impact strength,
- Evaluation of a wide range of physical properties of the above-mentioned set of random copolymers:

    - Density
    - Permeability
    - Transparency
    - Linear Thermal Expansion
    - Thermo-oxidative Stability
    - Solvent Absorption
    - Electrical Properties
    - Thermal Conductivity.

1.3.5 Commercial scale-up of polymer production

Following the result of successful bench-scale preparation in the gas-phase and exciting properties exhibited by propylene / 1-pentene random copolymers, a study was initiated to determine the feasibility of commercialising these polymers.

The feasibility study included carrying out a pilot-plant trial on an 800-liter reactor in Germany. The gas-phase pilot plant is a replica of Sasol's 50m^3 Novolen gas-phase plant in Secunda. During this two-week trial a range of propylene / 1-pentene random copolymers was produced. The 17 tons of material produced was shipped to South Africa and used to conduct a market acceptance study on various applications.

The information obtained from the pilot-plant trial in combination with the results of computer simulations was used to plan the first production run on a world-scale 50m^3 gas-phase plant. Modifications to the plant and the results from the commercial production run are discussed.

1.3.6 Application study

An extensive scientific study was conducted to determine the best potential applications for this exciting new family of propylene random copolymers. The propylene / 1-pentene random copolymer was evaluated for the following commercial applications:

- Films
    - Cast
    - Biaxially Orientated PP (BOPP)
- Injection moulded articles
- Blow moulded articles
- Thermoforming.

1.3.7 Summary

The commercial potential of propylene / 1-pentene random copolymers is analysed, based on the results obtained during this research project. This includes an overview of the commercial future of propylene / 1-pentene random copolymers, both from a market and production perspective.

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CHAPTER 2

HISTORICAL OVERVIEW OF PROPYLENE POLYMERS

2.1 EARLY DEVELOPMENTS

Although polyethylene (PE) was first synthesised in 1898 [1] and two years later identified as having a molecular structure corresponding to $(CH_2)_n$ [2], it was not until the 1920s that the importance of molecular weight of polymers and their chain structure were first recognised. In 1934 Fawcett and Gibson [3] reported on the formation of PE whilst researching the high-pressure chemistry of organic compounds. This led to the first patent [4] for the high-pressure production of PE in 1937 and the commissioning of the first commercial plant in 1939 by ICI [5].

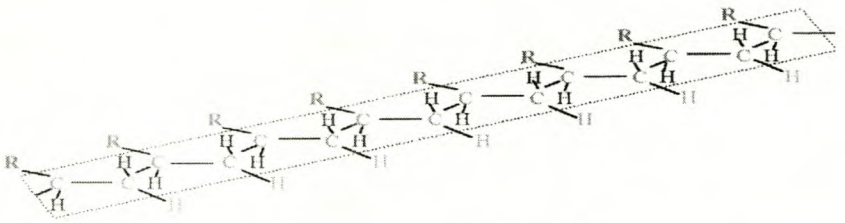
The absence of crystallinity in vinyl polymers, including polypropylene (PP), synthesised by radical polymerisation, as first pointed out by Staudinger [6], led to a renewed focus on the concept of stereo-regular polymerisation by leading researchers. In 1942 Bunn [7] published a paper predicting the helical form of PP, to be confirmed only in 1955 by Natta [8].

Ziegler and Gellert, because of experimental advantages, switched the focus of their research programme from lithium alkyls to trialkylaluminium catalysts [9,10]. In 1953 Ziegler [11] discovered that linear ethylene polymers with high molecular weight were obtained by the addition of a transition metal salt (e.g. $TiCl_4$) to the alkyl-aluminium catalyst.

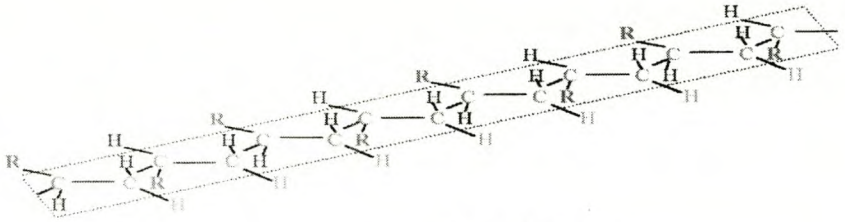
Before publishing his work, Ziegler disclosed his findings to the Italian chemical company Montecatini. Professor Natta of the Polytechnic Institute, working as a consultant for Montecatini, started investigating Ziegler's catalyst in 1952 [12]. In March 1954, using a $TiCl_4/Al(C_2H_5)_3$ catalyst, Natta and his co-workers obtained a rubber-like polymer of propylene [13]. Fractionation by solvent extraction exposed a highly crystalline powder, representing 30 to 40% of the total polymer, with a melting point of above 160 °C.

Initially the different properties of the fractions were attributed to different molecular weight fractions. However, crystallographic investigations led to the concept of tacticity. The soft, rubbery material, with an irregular structure, was labelled atactic PP and the crystalline material, with regular structure, labelled isotactic PP [14]. Natta also went on to define the third stereo conformation of PP, namely syndiotactic PP. The three identified stereo conformations of PP are shown in Figure 2.1.

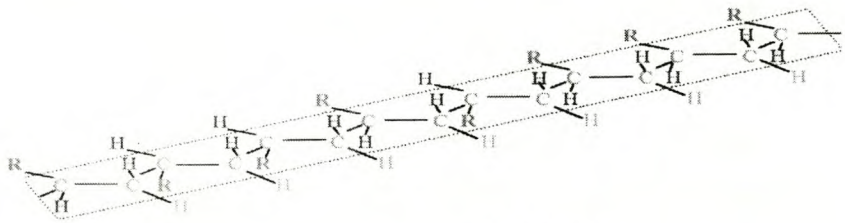
The advent of stereoregular polymerisation of propylene resulted in huge investments by major chemical companies allocating resources to the development of new chemistry, new production processes and products. Although crystalline PP was still only a dream in 1950, there were several commercial producers of PP in 1960, with a world production capacity in excess of 50 000 tons per annum [5].



Isotactic



Syndiotactic



Atactic

Figure 2.1: Polypropylene stereoisomers (R = CH^3)

2.2 CHRONOLOGICAL DEVELOPMENT OF ZIEGLER-NATTA CATALYSTS

2.2.1 Introduction

The discovery of transition metal catalysts for olefin polymerisation by Natta in 1954 made possible the synthesis not only of stereoregular olefin polymers, but also that of olefin copolymers. Natta's discovery opened the floodgates of scientific and industrial research. The focus of the research was mainly aimed at:

- Improving the activity of Ziegler-Natta catalysts, in other words the amount of polymer produced per gram of catalyst used,
- Improving the stereospecificity of Ziegler-Natta catalysts, in other words decreasing the ratio of atactic (amorphous) to isotactic (crystalline) material produced.

According to Galli et. al. [15] the historic development of stereospecific catalysts can be grouped into two main periods.

- The first period, during which most of the research efforts focussed on $TiCl_3$-based catalysts, the so-called *first generation* catalysts, originally developed by Natta and co-workers. This was followed by the commercialisation of a number of *second generation* catalysts, also based on $TiCl_3$, but modified with organic additives.
- The second period, during which research was focussed on developing high yield and high stereospecific catalysts. This resulted in the commercialisation of third and fourth generation catalysts, which are supported on $MgCl_2$, with a diester as an internal base and a silane as external base.

2.2.2 First generation Ziegler-Natta catalysts

The first PP produced by Natta and co-workers in a laboratory environment using a $TiCl_4$ / AlR_3 catalyst system only contained about 40% isotactic PP and could not be used as such for the commercial production of PP. The first important advance in the development of a catalyst system suitable for the commercial production of PP was the discovery that a $TiCl_3$ / AlR_3 or $TiCl_3$ / AlR_2Cl catalyst system was able to produce PP with a 90% isotactic content [16]. The catalyst system consisted of crystalline $TiCl_3$ mostly in the δ-form, prepared by the reduction of $TiCl_4$ with hydrogen, suspended in a hydrocarbon medium and treated with trialkylaluminium or dialkylaluminium-chloride.

Industrial research at Esso Research and Engineering Company [17] soon discovered that mixing the finely milled solid, obtained from prolonged ball milling of mixtures of $TiCl_3$ and $AlCl_3$ with aluminumalkyls, gave a catalyst of higher activity. Tornqvist and his coworkers showed that the ball-milling process converted the combination of α, γ and δ forms found in $TiCl_3$ to almost exclusively the δ form. The productivity and stereospecificity of this catalyst system was, however, still rather low, requiring the removal of both catalyst residues and separation of part of the atactic fraction [18]. This made the commercial production of PP complicated and expensive.

2.2.3 Second generation Ziegler-Natta catalysts

A further improvement in catalyst stereospecificity was achieved by adding a Lewis base (donor) to the crystalline $TiCl_3$. The selected donors generally are esters, ethers, amines or phosphorous organic derivatives. The use of Lewis bases to enhance catalytic activity was first proposed by Razuvaev and co-workers [19]. Coover and co-workers, however, were the first to prepare active catalyst systems from $TiCl_3$, AlR_2Cl and a Lewis base [20].

According to Galli et. al. [15] the role of the Lewis bases in improving the stereospecificity of Ziegler-Natta catalyst systems can be summarised as follows:

- Selective poisoning of the more exposed and less stereospecific active catalyst centres,
- Removal of poisonous substances from the catalyst surface through a complexing process,
- Stabilisation of the active centre structure and chirality,
- Decreasing the reduction power of the $TiCl_3$.

These compounds are often ball-milled together with the δ- $TiCl_3$-0.33 $AlCl_3$. Because factors such as mode of addition, temperature, concentration and the nature of the donor influence catalyst performance, most companies have their own recipes [21]. However, even with the improvement in stereospecificity and activity (3 to 5 times higher) of the catalyst systems, purification of the PP from excessive catalyst residues was still required during the manufacturing process [22].

2.2.4 Third generation Ziegler-Natta catalysts

In parallel to the developments described in Section 2.2.3, a series of attempts was made to support the titanium catalyst on carrier materials. This was done in recognition of the fact that the concentration of active sites compared to the total titanium content was very low. These attempts, however, though leading in some cases to highly active catalysts for PE, were not very successful for PP [23]. It was only when activated $MgCl_2$ was introduced as support that catalysts with activities of up to 200 times that of typical second generation $TiCl_3$-based were achieved. The isotactic content of these propylene polymers, however, was extremely low – between 20 and 50% [24].

The success of $MgCl_2$ can be attributed to a number of factors. The first is the fact that $MgCl_2$ has a crystalline form similar to $TiCl_3$ [25]. $MgCl_2$ as a support also has a structure that can resist particle break-up during handling but is still weak enough to disintegrate during polymerisation. This is critically important to expose more active sites and enhance the activity of the catalyst. In addition $MgCl_2$ has a lower electronegativity compared to other metal halides and is inert [26], making the de-ashing step redundant - as the $MgCl_2$ can be left in the polymer.

The problem of low stereospecificity was solved by the addition of appropriate Lewis bases [27]. This was achieved by co-milling $TiCl_3$, $MgCl_2$, a trialkylaluminum as co-catalyst and a Lewis base as internal donor, in combination with a second Lewis base as external donor [26, 28]. It was proposed by Busico et. al. that the internal donor prevents $TiCl_3$ from co-ordination on the $MgCl_2$ crystal faces, where mostly non-stereospecific active sites would be formed [24]. It was also reasoned that the external donor selectively inhibits non-stereospecific catalyst centres.

2.2.5 Fourth generation Ziegler-Natta catalysts

The third generation catalysts did, however, have two major drawbacks, namely [29]:

- The Lewis bases, being aromatic esters, left some tenacious odours in the final product,
- The catalyst system was relatively unstable at temperatures above 70°C.

These drawbacks led to the development of a new type of Ziegler-Natta catalyst systems employing a silane compound as external base. The catalyst system comprised a diester (e.g. dibutyl phthalate) as an internal weak Lewis base and a silane (e.g. triethoxy-phenylsilane) as an external Lewis base [30,31]. The catalyst system described above is currently used in most of the modern industrial processes for PP manufacturing. Compared to third generation catalysts they offer the following advantages, namely:

- High isotacticity obtained with a low aluminium to Lewis base ratio,
- Stereospecificity is stable with temperature,
- Sensitivity to hydrogen is high,
- Activity is greatly enhanced by the transfer agent, namely hydrogen.

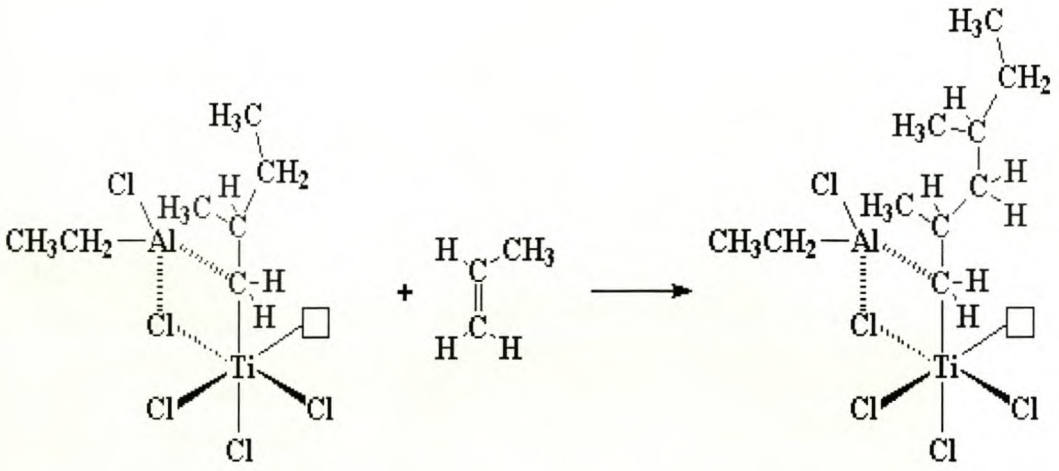


Figure 2.2: Typical Ziegler-Natta polymerisation mechanism

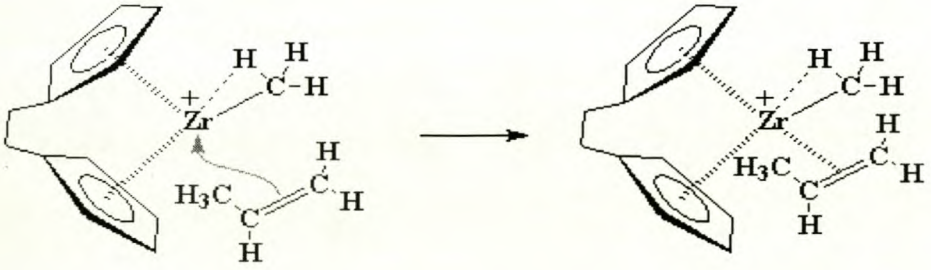


Figure 2.3: Typical Metallocene polymerisation mechanism

2.2.6 Fifth generation catalysts (metallocenes)

A number of research groups [32,33] have reported that stereorigid metallocenes of transition metals such as Zr and Hf, when combined with methylaluminiumoxane (MAO), are capable of producing highly stereoregular isotactic or syndiotactic polypropylene. With these catalyst systems it is possible to achieve extremely high yields, narrow molecular weight distributions and homogeneous co-monomer distribution along the polymer chain. The high activities achieved ensure a product with much improved organoleptic properties.

Metallocene catalysts for propylene polymerisation have a sandwich-type arrangement in which the transition metal is in the middle of two cyclopentadienyl (Cp) groups. The Cp groups can be the same or different but the overall symmetry of the arrangement determines whether the catalyst will produce isotactic or syndiotactic polymer.

Metallocenes have been a very significant breakthrough for commercial catalyst technology [34]. These new catalysts will most probably have the same impact on the polymer industry as the development of fourth generation Ziegler-Natta catalysts. Metallocene catalyst systems are compatible with modern polymerisation processes and no major modification costs are required. However, metallocene catalysts require a new co-catalyst, namely methyl aluminoxane (MAO), which is used at much higher levels than for co-catalysts in fourth generation systems, making metallocene-produced PP more expensive.

2.3 POLYPROPYLENE

2.3.1 General

The story of polypropylene is really the story of its catalyst. The extraordinary progress made in catalyst understanding and, in particular, the correlation between catalyst structures and polymer properties, significantly enhanced the versatility of production processes and the range of polymer properties. The recent advances in catalyst technology have revolutionised PP production, allowing a substantial simplification of processes which has had a huge impact on economics [35]. As such it is no surprise that PP has the highest production volume of all olefin polymers in the current world market.

Polypropylene is an extremely versatile polymer that is encountered in many areas of everyday life. The market interest in polypropylene lies mainly in its excellent thermal and chemical resistance, good mechanical properties and facility for transformation. Isotacticity and crystallinity are two fundamental properties of PP. By using the right catalyst and production process, and the introduction of co-monomers, it is possible to fabricate a polypropylene-based polymer which has tailor-made properties, such as: mechanical, physical and thermal properties e.g. stiffness, melting point, impact strength, transparency etc. [36].

There are three main families of PP commercially available today, namely:

- **Homopolymers** - Highly crystalline PP homopolymers are stiff, tough above 0°C, and have high heat-distortion temperatures. They are useful for a wide range of applications such as fibres, films, pipes and a host of injection and blow moulded items [5]. However, PP homopolymers do have some drawbacks, namely, brittle behaviour below 0°C, rigidity and poor transparency and melt strength.

- **Impact (block) copolymers** – Impact copolymers, also known as heterophasic copolymers, usually contain up to about 60% ethylene-propylene rubber (EPR), intimately dispersed within the homopolymer matrix [37]. To produce this family of PP copolymer, two reactors in cascade are required, with the second reactor always a gas-phase reactor. By polymerisation of propylene (first reactor) followed by co-polymerisation of propylene with ethylene (second reactor), a PP-matrix is formed with embedded particles of ethylene-propylene rubber (two-phase material). Although PP impact copolymers exhibit very good low-temperature impact strength and the same high melting temperature than that of PP homopolymer, they are opaque with lower stiffness and hardness.

- **Random copolymers** – Random copolymers typically contain up to 6% (by weight) of ethylene or other comonomers, inserted at random within the polymer backbone. This reduces the crystallinity and the melting point by introducing irregularities into the polymer chain. Random copolymers are used where clarity, lower melting point, or lower stiffness is desirable. In the context of the focus of this research project the next section deals with PP random copolymers in more detail.

2.3.2 Propylene / α-olefin random copolymers

The family of random co- and ter-polymers was identified during the Polypropylene '92 World Congress as a solution for extending the limits of PP properties [36]. Most commercially available propylene copolymers have ethylene as comonomer, although some contain 1-butene [38]. There are also a number of terpolymers containing ethylene and 1-butene. The typical ethylene content is between 1,5 and 6% by weight, but values as high as 7% and even 12% have been reported [39]. The typical 1-butene content, however, is between 5% and 15% and imparts a higher modulus, higher melting point, lower extractables and lower haze to the copolymers compared to ethylene randoms [36,40]. One of the most interesting random copolymers described in the literature contains 1-hexene as comonomer [35]. These random copolymers exhibit higher impact strength, clarity and modulus than ethylene copolymers do.

According to definition, random co-polymerisation is the reaction between two monomers where there is an equal preference for either monomer to add to the growing chain. However, as pointed out by Kissin [41], the comonomer

reactivity appears to decrease with increasing the steric hindrance around the double bond in the following order:

Ethylene > Propylene > 1-Butene > Linear α-Olefins > Branched α-Olefins

As such, all centres that polymerise 1-butene will also be active for propylene and the more so for ethylene but not vice versa [42]. However, there are several registered patents describing the copolymerisation of propylene with 1-butene and 1-hexene using third and fourth generation catalysts [43, 44, 45, 46]. Some relative co-polymerisation activities of linear α-olefins to propylene are: 0,5 – 0,6 for 1-butene [47], 0,2 – 0,5 for 1-pentene and 0,2 – 0,4 for 1-hexene [48].

The randomness of a copolymer refers to the dispersion of the comonomer units along the propylene chain. The number of interruptions of the stereoregular polypropylene sequence controls the properties of the random copolymer. This implies that a high dispersion of the comonomer units improves the efficiency of the incorporated comonomer in affecting the copolymer properties.

Theoretically it can be argued that when the product of the reactivity ratios of the respective copolymers (r_1*r_2) approaches unity, the copolymer shows a random structure. In the instance where the product of the reactivity ratios is greater than 1 a block-like microstructure is obtained, as is an alternating structure obtained for values smaller than 1. Detailed investigations carried out on propylene random copolymers with ethylene [49], 1-butene [50] and 1-hexene [51], all prepared with fourth generation catalysts, point towards a random structure.

Many researchers have reported an increase in polymerisation rate when propylene is copolymerised with small amounts of ethylene, both with third and fourth generation Ziegler-Natta catalysts [52,53]. In the copolymerisation of propylene with 1-butene there is no clear relationship reported between catalyst activity and comonomer content [54] but for 1-hexene and heavier α-olefins propylene reactivity increases with comonomer content [51].

2.3.3 Global production capacities

The year 1954 heralded the discovery of crystalline propylene polymers. It was a significant step forward - from low molecular weight irregular oligomers to high molecular weight polymers with a high crystalline content. Since the first Montecatini PP plant in Italy went into production in 1957, followed shortly thereafter by the start-up of the second PP plant by Hercules in the U.S.A., we have seen exponential growth in the world wide PP production capacity, as illustrated in Figure 2.4 below [55, 56].

Also shown below is the growth in PP production capacities in the major producing regions in the world. The growth rate in the Asia Pacific region and the developing world far outperform that of the traditional leaders in the developed world.

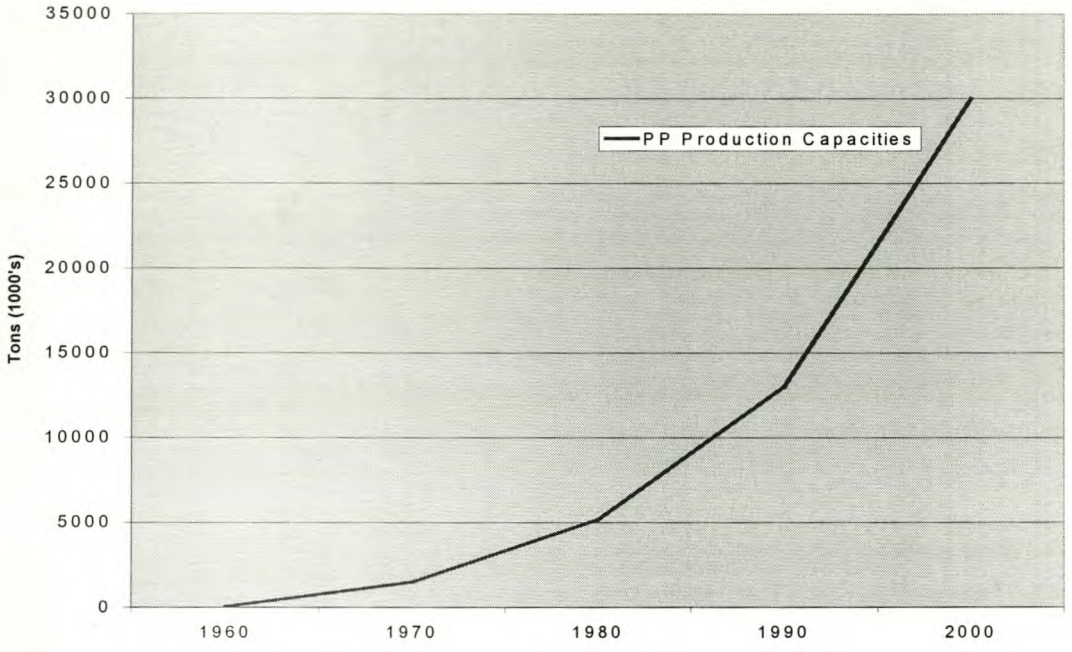


Figure 2.4: World-wide PP production capacities

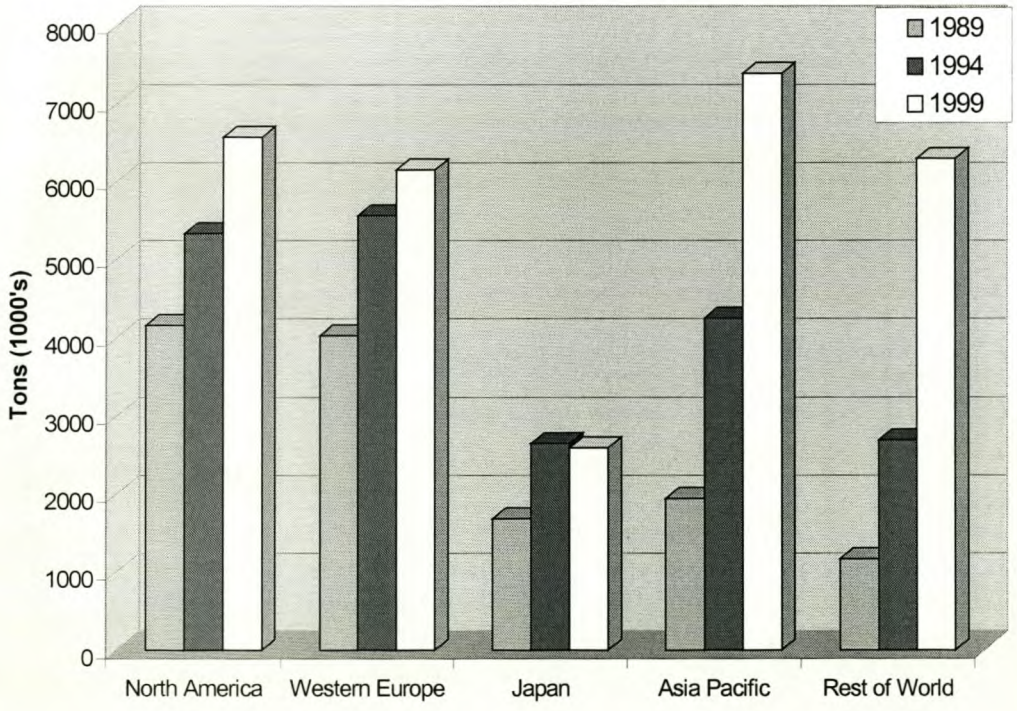


Figure 2.5: Development of regional PP production capacities

The world growth rate for PP during the 90's has dropped to below double-digit figures and product differentiation is seen as the only way forward for the industry [38, 39, 55]. Although the usage of PP random copolymers is currently only about 6% of the total PP usage, this family of PP polymer was identified as one of the most important solutions by which to extend the limits of PP properties and as such it is expected that we will see huge growth in the market share of random copolymers.

2.3.4 Commercial polymerisation processes

2.3.4.1 Introduction

Commercial propylene polymerisation processes today can be divided into four basic categories, namely [5]:

- Slurry polymerisation processes – in hydrocarbon suspension
- Bulk polymerisation processes
- Gas-phase polymerisation processes
    - Fluidised bed
    - Horizontal stirred bed
    - Vertical stirred bed
- Combination of bulk and gas phase.

Most improvements in industrial propylene polymerisation processes over the years were as a result of developments in catalyst systems. Knowledge and control of the polymerisation process determines not only process economics, but also materials produced, the property envelope and potential market applications. The relationship between catalyst capabilities, the polymerisation process and final product properties is widely recognised.

The four most popular technologies, shown in Figure 2.5 below, are given special attention in the following sections. Because of the similarities between the Basell and Borealis technologies only the Basell technology is discussed. Due to its historic significance an overview of the slurry process is also given.

2.3.4.2 Slurry polymerisation processes

The first industrial polymerisation process, utilising slurry technology, was developed by Montecatini and commercialised in 1960 [57]. The limitations of the early Ziegler-Natta catalyst systems with regard to activity and tacticity necessitated the removal of catalyst residues and an excessive atactic content. As such, the first semi-batch polymerisation processes required the use of a hydrocarbon diluent, hexane or heptane, to suspend the crystalline PP produced and dissolve the atactic (amorphous) polymer fraction [58].

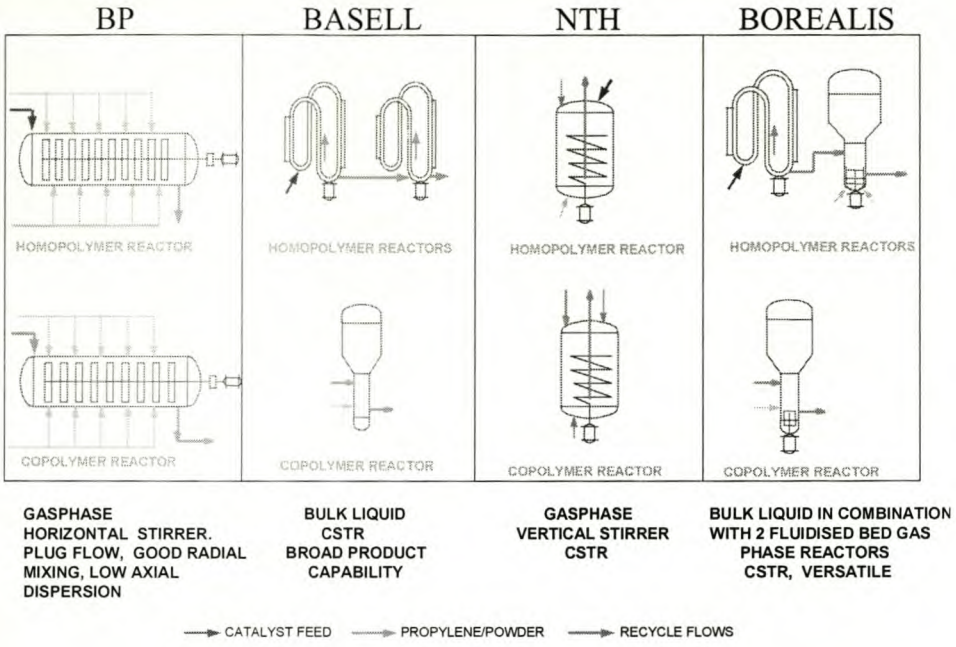


Figure 2.6: Schematic representation of production processes

After polymerisation and degassing, the polymer slurry was treated with alcohol, followed by treatment with caustic to neutralise the HCl formed during the initial treatment to neutralise the catalyst. The aqueous and hydrocarbon phases were separated and the suspended crystalline polymer separated from the hydrocarbon diluent by filtration or centrifugation.

The slurry process is no longer cost competitive, even with the use of high-activity catalyst systems, and also presents serious limitations in the production of impact and random copolymers due to the increased solubility in the hydrocarbon diluent. However, the amorphous PP by-product is desirable for certain applications and at least one plant has been converted to produce exclusively amorphous PP [59].

2.3.4.3 Basell polymerisation technology

The second process to be developed for the production of PP used liquid monomer as the polymerisation medium in a continuously stirred tank reactor (CSTR). This process, pioneered by Rexall [60] and Phillips [61], had two major advantages over the slurry process, namely [62]:

- Higher polymerisation rates as a result of higher monomer concentrations,
- Elimination of the purification and recycling of the hydrocarbon diluent simplified the production process.

Modern industrial processes using liquid monomer as the polymerisation medium can be divided into two categories, namely those using continuous stirred reactors and those using loop reactors. Use of the loop reactors shown in Figure 2.6 (licensed by Basell) is the preferred technology for economic

reasons [63]. Because of the small diameter of the loop reactors, typical operating pressures do not require excessive wall thickness.

The Basell loop reactors can produce a wide range of propylene homopolymers and random copolymers. However, it is not possible to produce random copolymers with comonomer content (ethylene) exceeding 5%, due to their high solubility in liquid propylene [5].

Typical operating conditions for the loop reactors are in the range of 60 to 85°C and 35 to 50 bar [64]. Catalyst and co-catalyst are pre-mixed before the catalyst mixture is mixed with chilled liquid propylene. This mixture is then fed to a small loop reactor with additional propylene to facilitate controlled pre-polymerisation under mild conditions. After a short residence time in the pre-polymerisation reactor the catalyst mixture is fed into the main loop reactor.

The slurry in the reactor, with a polymer density of 50 to 55% by weight, is circulated at high velocity through the loop reactor ensuring uniform mixing. The heat of the reaction is uniformly removed by circulating water through the jacket of the loop reactors. Polymer slurry from the first reactor is fed directly to the second reactor to complete the polymerisation process. Polymer slurry from the second reactor is continuously discharged through a steam-jacketed pipe, so as to ensure monomer evaporation.

For the production of impact polymers (block copolymers) the slurry from the second loop reactor is depressurised and flashed to vaporise residual monomer before being fed to a fluidised bed gas-phase reactor to produce the ethylene-propylene rubber phase [65]. The gas-phase reactor typically operates at 14 bar, 80 to 85°C with a bed density of 300 to 350 kg/m^3 and residence time of 0,3 hours. The final polymer product is discharged through the bottom of the reactor, the monomer is separated and the catalyst deactivated.

2.3.4.4 BP polymerisation technology

In the mid-1970s the horizontally stirred, multistage gas-phase process was developed by BP for homopolymer only and in 1987 expanded to include ethylene-propylene impact copolymer production [5]. This gas-phase process is unique in the polypropylene industry in that it approaches plug-flow type of performance with only one reactor. However, for the production of impact copolymers two reactors are still needed [66].

Polymerisation takes place in a horizontal reactor gently agitated by a mechanical stirrer. The heat of polymerisation in the reactor is removed by evaporative cooling, which is the most effective method of heat removal (utilising the heat of evaporation). Evaporative cooling is accomplished by liquid propylene being sprayed onto the reactor powder bed and vaporised inside the reactor. This cooling method is more effective and efficient when compared to heat removal by sensible cooling of a gas stream (fluidised bed reactors) or by indirect cooling via heat transfer surface (jacketed reactors e.g. Basell loop reactor).

The BP reactors have a very high space-time-yield (production rate per unit reactor volume) ratio. Due to the plug-flow characteristics of the reactor the grade transition times of the BP reactors are shorter (theoretically) than that required for continuous stirred tank reactor or fluidised bed reactor processes.

2.3.4.5 NTH polymerisation technology

BASF pioneered gas-phase polymerisation processes by introducing the Novolen stirred-bed process in 1969 [67, 68]. The recent introduction of high yield, high stereospecific catalyst systems eliminated product deficiencies by reducing the atactic and residual catalyst content in the polymer produced. Polymerisation is performed in vertically stirred reactors, one reactor for the production of homopolymer and random copolymer and two reactors for the production of impact copolymers.

Propylene is fed as a liquid, both from the bottom and the top, to the polymerisation reactor. The reactors have an excellent space-time-yield ratio, allowing compact plant design. Typical polymerisation temperatures range between 50 and 90°C and the pressure between 10 and 40 bar. As with the BP process, the heat of evaporation of the liquid monomer is used to facilitate heat removal in the reactor as the polymerisation process is exothermic. Gas from above the polymer powder bed is recycled and condensed before being re-introduced into the reactor.

A mixture of polymer powder, monomers and hydrogen is discharged from the reactor through dip legs. Adjusting the length of pulse and / or frequency of the discharge valves controls the discharge rate, maintaining the bed height at a constant level. The polymer and carrier-gas are separated in the discharge vessel and the carrier gas, normally about 20%, recycled.

2.3.5 Properties and applications

Polypropylene is an extremely versatile material with an interesting combination of properties. Listed below are some of the characteristics that have resulted in the phenomenal and sustained growth enjoyed by PP over the last 4 decades [5, 37, 38]:

- High performance-to-cost ratio
- PP is a lightweight material with a density of 0,9 g/cm^3
- A relative high flexural modulus and melting point are the two properties that sets PP apart from other polyolefins
- Exhibits excellent chemical resistance
- Good optical and gloss properties of films
- Weld and sealability
- Toughness.

PP can also be copolymerised with other monomers or alloyed with other polymers to yield final products custom-designed for specific applications. Although PP homopolymers exhibit poor impact strength below 0°C, good impact strength is obtained at temperatures as low as –40°C with

heterophasic impact copolymers. Random copolymers, on the other hand, offer improved impact strength, transparency, gloss, heat seal initiation temperatures and melt strength above homopolymers [69]. The typical property range of commercially available PP homo- and co-polymer grades is summarised in the table below.

Table 2.1: Typical Property Profile of PP Homo- and Copolymers

Polymer Property	Unit of Measure	ASTM Test Method	Value Range
Melt Flow Ratio (MFR)	g/10'	D1238/L	0,3 – 100
Flexural Modulus	MPa	D790	700 – 2350
Notched Izod (23°C)	J/m	D256	30 – 750
Rockwell Hardness	"R"	D785	84 – 112
Vicat Softening Point (10N)	°C	D1525	116 – 159
Tensile Strength at Yield	MPa	D638	22 – 41
Elongation at Yield	%	D638	5 – 15
Haze	%	D1003	1,4 – 32*
Heat Deflection Temperature (0,46 N/mm^2)	°C	D648	65 – 128

* Only homopolymer and random copolymer

The major applications for PP and its copolymers are listed below, with a brief description of each [5, 37, 70].

- Extrusion applications:
  - Fibre
  - Raffia
  - Cast film
  - Blown film
  - Bi-axially orientated (BOPP) film
  - Pipe
  - Non-Woven

- Injection-moulding applications
  - Domestic ware
  - Automotive
  - Medical

- Injection stretch blow-moulding applications
  - Containers

- Blow-moulding applications
  - Cosmetic containers
  - Pharmaceutical
  - Beverage

- Thermo-forming applications
  - Agricultural
  - Food packaging

Tabulated below are the current volumes of polypropylene usage per major producing region per application [71].

Table 2.2: PP volumes per application per region

	Western Europe	**Japan**	**USA**
Extrusion			
Fibre	1202	90	
Raffia	397	57	1643
Film	1318	486	555
Other	356	203	211
Injection Moulding	2790	1284	1792
Blow Moulding	90	112	86
Other	0	36	1503

From the table it is obvious that injection moulding, extrusion of fibre and fibre applications still dominate the PP market. The main application area for PP random copolymers is in the extrusion sector. However, PP random copolymers with improved transparency, gloss, and melt and impact strength will open new applications in especially the injection moulding, blow moulding, BOPP and thermo-forming sectors of the industry [69].

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CHAPTER 3:

PREPARATION AND CHARACTERISATION OF RANDOM COPOLYMERS OF 1-HEXENE AND 1-PENTENE WITH PROPYLENE AT AMBIENT PRESSURE

3.1 INTRODUCTION

The first phase of this research project was to develop and gain experience in bench-scale polymerisation techniques, at ambient pressure [1], that could produce PP polymers that showed good correlation with a typical commercial grade of PP produced by SASOL POLYMERS. Two batches of propylene homopolymer were prepared using a 1-liter, four-neck glass reactor in a fumehood. Heptane was used as solvent in the first reaction and toluene in the second. A typical second generation Ziegler-Natta catalyst [2], the reactivity during a pressureless solution polymerisation as yet unknown to us, was used. Initially only a very small amount of catalyst was used.

The second phase of the research project was to develop bench-scale polymerisation techniques to prepare random copolymers of propylene with 1-hexene and 1-pentene respectively. The comonomers of choice for the production of propylene random copolymers are ethylene and 1-butene, with ethylene mostly used in commercial production processes [3].

The change in the relative comonomer concentrations in the reactor with time, due to the huge difference in reactivity ratios, was also investigated. For the linear α-olefins, activity generally decreases with increasing chain length as can be seen from Table 3.1 [4]. The reactivity ratios of the branched olefins 4-methyl-1-pentene (4MP1) and 3-methyl-1-pentene (3MP1) are also given.

Table 3.1. Reactivity ratios of α-olefins relative to propylene

Monomer	C_2	C_3	C_4	C_5	C_6	C_{10}	4MP1	3MP1
Relative Reactivity	20 - 8	1	0.62-0.22	0.45-0.2	0.36-0.16	0.28-0.12	0.15	0.048

3.2 PREPARATION OF PROPYLENE HOMOPOLYMER (PP)

3.2.1 Experimental set-up

All glassware was thoroughly washed, dried at 120°C, and assembled while still hot. The polymerisation process commenced after the equipment had cooled in a nitrogen atmosphere.

Solvents were dried over molecular sieve (5Å) for at least 48 h prior to use, then degassed under vacuum, followed by purging with nitrogen. The reaction vessel was charged with 700 ml solvent under nitrogen.

The reaction set-up used is shown in Fig 3.1. It comprised a 1-liter, four-neck jacketed flask, equipped with stirrer, thermometer, a propene and a nitrogen inlet, and a gas outlet tube fitted with a stopcock. The propene and nitrogen inlet was fitted with a 3-way stopcock. The jacketed reaction vessel was connected to a water bath with an automatic temperature controller.

Both the nitrogen and propene inlet tubes as well as the gas outlet tube were connected to bubblers. The bubblers were filled with the same solvent used for the polymerisation process. To purify the nitrogen and propene, 5 ml diethylaluminiumchloride (DEAC) was added to the solvent, bubblers, using a gas-tight syringe.

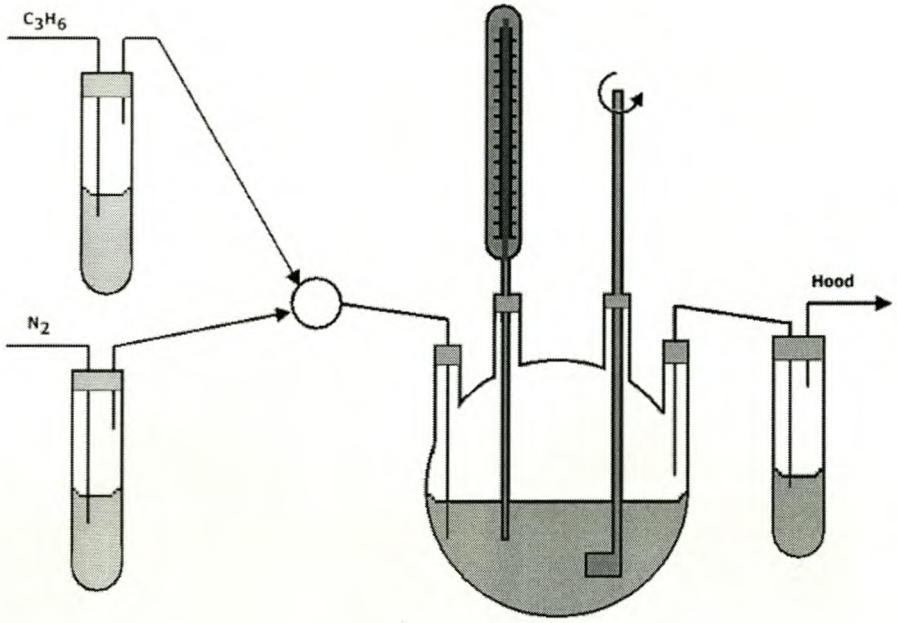

Fig 3.1: Set-up used for the polymerisation of propylene in slurry, in a glass reactor

3.2.2 Polymerisation procedure

The correct amount of DEAC was weighed off in a gas-tight syringe and introduced to the reaction vessel via the septum seal. The correct amount of solid catalyst was then weighed off in a small glass tube under a nitrogen blanket. All catalyst manipulations were carried out in a Mbraun model MB 150 glove-box containing a nitrogen atmosphere with water levels below 0.2 ppm and oxygen levels below 1 ppm.

The thermometer was removed and the solid catalyst introduced directly into the reaction vessel. The catalyst was protected against oxygen and humidity in the air by means of slight positive nitrogen pressure in the polymerisation

vessel. The thermometer was replaced immediately after the addition of the solid catalyst.

The water-bath temperature was set at 60°C. At 50°C the changeover from nitrogen to propylene was made. A polymerisation temperature of 60°C was maintained throughout the polymerisation process. The propylene flow was adjusted such that a small gas flow was visible through the bubbler connected to the outlet tube. Frequent readjustments of the flow rate were necessary due to changes in the uptake of the PP during the polymerisation process.

3.2.3 Termination and precipitation

The water bath was switched off and the gas supply changed from propylene to nitrogen. To terminate the polymerisation process about 50 ml methanol was slowly added to the reactor. This caused the reaction mixture to turn white at once. The polymer was filtered with suction and washed with a 25% mixture of HCl in methanol, followed by consecutive washes of methanol and acetone. The polymer was dried for 12 h in a vacuum at 60°C.
The polymerisation flask was disconnected from the rest of the apparatus. The stirrer and contact thermometer were cleaned immediately.

The conditions and catalysts/co-catalysts used in the two reactions were the following:

Reaction 1

Reaction conditions:

Time	19 h
Pressure	Ambient
Temperature	60ºC
Solvent	(Heptane (700 ml))
Al / Ti*	4

* (mol ratio of Al in DEAC to Ti in catalyst)

Catalyst
0,02 g of the second-generation ball milled Ziegler Natta catalyst mixture was used. It consisted of 1/3 mol stereo-modified n-propyl benzoate for every 1 mol Ti Cl_3.0,33 $AlCl_3$.

$$= \frac{198{,}26}{198{,}26 + 1/3\ (164.20)} \times 100$$

= 78,365% $TiCl_3$.0,33 $AlCl_3$ in mixture

= 0,02 * 0,784 = 0,0157 g $TiCl_3$.0,33 $AlCl_3$ added.

Cocatalyst
DEAC needed for Al/Ti ratio = 4:

$$= 0{,}0157 \times \frac{\text{MM DEAC}}{\text{MM Cat}} \times 4$$

= 0,0382 gram DEAC

DEAC mixture however consists of:

Heptane	7,95 kg
Irganox 1076*	0,80 kg
Et_2AlCl (DEAC)	1,25kg
	10,00 kg

* (added as stabiliser)

= 0,0382 * 10 / 1,25
⇨ 0,305 gram of mixture needed (for Al / Ti = 4).

Reaction 2

Reaction conditions:

Time	110 min
Pressure	Ambient
Temperature	65°C
Solvent	Toluene (700 ml)
Al / Ti*	4

Catalyst
0,5 g of the second generation milled Ziegler-Natta catalyst mixture was used.

= 0,5 * 0,784
⇨ 0,392 g $TiCl_3$.0,33 $AlCl_3$.

Cocatalyst

= 0,953 g DEAC
⇨ 7,628 g of DEAC mixture

3.2.4 Results

The two batches were analysed with respect to the following properties and the results tabulated below:

- Melt flow index (MI)
- Isotacticity, by nuclear magnetic resonance spectroscopy (NMR)
- Peak melting points, by differential scanning calorimetry (DSC)
- Ti and Al residues, by atomic absorption (AA)

Table 3.2: Various properties of the two batches of PP prepared on laboratory scale, compared to a commercially produced batch (Sasol PP).

Property / Polymer	Melt flow index	Isotacticity (%)	Melting point (°C)	Ti residu (ppm)	Al residu (ppm)
Batch 1 PP	0,05	95,66	167	-	-
Batch 2 PP	1,80	79,25	162	9	125
Sasol PP	0,9 – 45	95,00	162	40	150

3.2.5 Discussion

The very small amount of catalyst used for the first reaction and the long reaction time allowed resulted in a PP product with a very low melt flow index, indicating a very high molecular weight (a high melt flow index indicates a low molecular weight polymer.) The isotacticity was 95,7%, which is typical of polymers produced by SASOL POLYMERS.

The second polymerisation reaction produced a polymer with a melt flow index of 1,8 and a melting point of 160°C, which is in good agreement with typical grades of PP produced by SASOL POLYMERS at the Secunda plant.

The change in isotacticity may be attributed to toluene used as solvent for the second polymerisation reaction compared to heptane used in the first reaction. The higher-than-normal melting point of batch 1 can be attributed to its very high molecular weight.

The catalyst residue (Ti and Al) in the second batch prepared was less than the residue in a typical batch produced by SASOL POLYMERS, indicating that the washing procedures followed were adequate.

3.3 COPOLYMERISATION OF 1-HEXENE AND PROPYLENE

3.3.1 Experimental

The copolymerisation of 1-hexene and propylene was carried out in slurry, using the same procedure and second generation Ziegler-Natta catalyst system as described in Section 3.2, but with between 11.5% and 14.5% of 1-hexene added to the heptane solvent. 1-Hexene was initially used as comonomer as the 1-pentene plant was still under construction. The objective of this exercise was twofold, namely:

- Determine whether a typical commercially available, second generation Ziegler-Natta catalyst system is capable of incorporating the bulkier 1-hexene (and by default 1-pentene) monomer into the polymer backbone, and
- Study the drift in the comonomer ratio with time during the copolymerisation of propylene and 1-hexene at ambient pressure.

The copolymerisation reactions were carried out at four selected catalyst to 1-hexene molar ratios, as indicated in the table below.

Table 3.3: Catalyst to comonomer ratio for copolymerisation reactions

Reaction Number	Titanium to 1-Hexene Molar Ratio
Reaction 1	0,006
Reaction 2	0,004
Reaction 3	0,003
Reaction 4	0,003

Samples of the reaction mixture were taken at selected intervals, by syringe through the septum seal, during the polymerisation process and analysed for the 1-hexene content.

3.3.2 Results

The propylene concentration was determined by the solubility of propylene in the reaction medium [5]. Due to the limited solubility of the propylene it is replenished during the reaction, resulting in a constant propylene concentration. As the 1-hexene is being consumed, a drift in the comonomer ratio occurs.

The results of the change in the relative 1-hexene concentration versus reaction time are presented graphically in Figure 3.2 below.

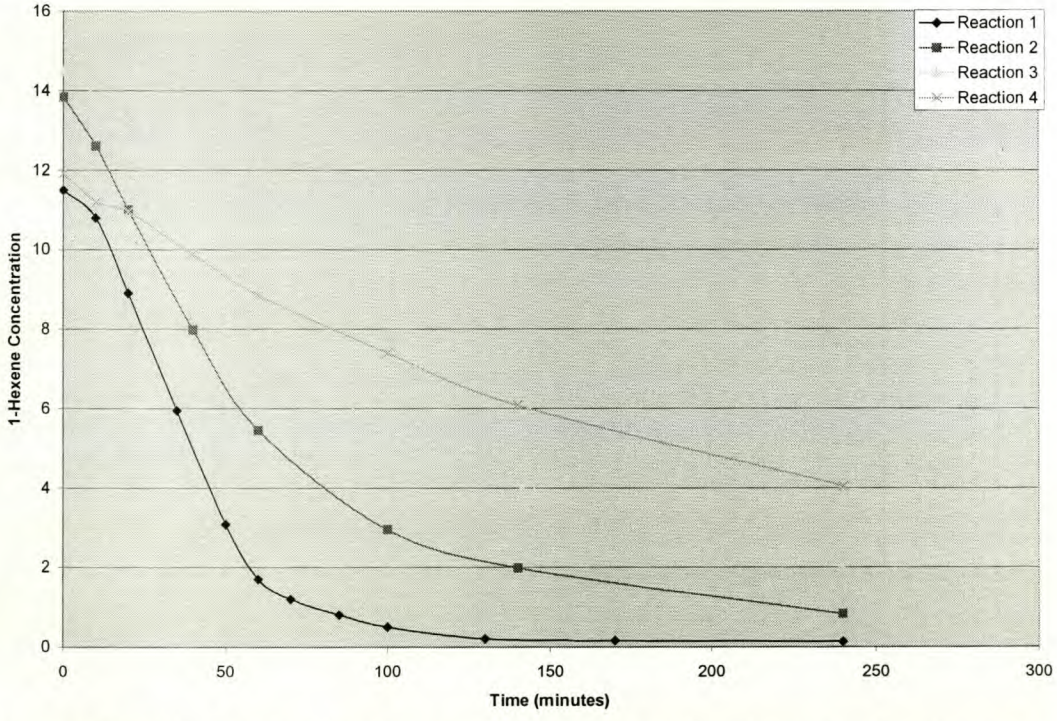

Figure 3.2: Change in 1-hexene concentration with polymerisation time

From the dramatic change in the relative 1-hexene concentration the following conclusions can be made.

- The commercially available, second generation Ziegler-Natta catalyst successfully incorporated the bulkier 1-hexene monomer into the polymer backbone.
- The drift in comonomer ratio is dramatic; about 50% of the 1-hexene is consumed during the first 30 minutes of the reaction.

3.3.3 Discussion

The seemingly easy incorporation of the bulky 1-hexene monomer into the polymer backbone suggests that the specified catalyst system should also be able to incorporate the 1-pentene monomer with propylene monomer into the polymer chain. However, the huge drift in comonomer ratio renders this polymerisation procedure not suitable for the preparation of random copolymers.

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CHAPTER 4

PREPARATION AND CHARACTERISATION OF RANDOM COPOLYMERS OF PROPYLENE WITH HEXENE AND 1-PENTENE RESPECTIVELY AT PRESSURES EXCEEDING VAPOUR PRESSURE OF PROPYLENE

4.1 INTRODUCTION

A range of propylene / 1-hexene and propylene / 1-pentene random copolymers was prepared and characterised. The copolymers were prepared in a 1-l autoclave, using the second generation $TiCl_3$,0,33$AlCl_3$-Et_2AlCl catalyst system [1]. The propylene / alpha-olefin comonomer ratio within the reactor was controlled by conducting the copolymerisation reactions at pressures exceeding the vapour pressure of propylene. To avoid heterogeneity in the composition of the copolymers the average conversion of the copolymerisation reactions was kept below 20%.

The copolymer compositions were determined by 1H NMR spectroscopy. The results were correlated with theoretical values obtained for the propylene / 1-hexene random copolymers by applying a set of published reactivity constants [2] to the copolymerisation equation as proposed by Alfry and Goldfinger.

The change in crystallinity and melting point with increasing 1-hexene content was studied by WAXD and DSC respectively. To complement this, the effect of incorporating 1-hexene into the polymer backbone on the crystal structure of the polymer, was investigated using light microscopy.

4.2 EXPERIMENTAL

4.2.1 Solvent and Monomer purification

ASTM grade n-heptane (Chemworld) was used as solvent for the polymerisation reactions. Prior to use, the solvent was distilled under nitrogen in the presence of triethylaluminium, and subjected to quality control. The monomers 1-hexene (from Fuel Research, Sasol) and propylene (Sasol Polymers) were used without purification. Both solvent and monomers were analysed with respect to its water and oxygenate content. The results are shown in the table below.

Table 4.1: Water and oxygenate levels in solvent and monomers.

Chemical	Oxygenates (ppm as MEK)	Water (ppm)
n-Heptane	<10	<20
1-Hexene	<10	<10
Propylene	<5	<10

4.2.2 Polymerisation procedure

All reactions were carried out in a 1-l jacketed Buchi reactor equipped with sight glasses, an anchor stirrer with a magnetic drive and a thermocouple at the base of the autoclave. The lid of the autoclave was fitted with the following connections:

- Ultra-high purity (UHP) nitrogen
- Feeding point for solvent and catalyst
- Cylinder with monomer mixture attached to a bottle of UHP nitrogen
- Vent line
- Pressure gauge

The monomer transfer cylinder was evacuated and subsequently filled with the correct quantity of 1-hexene before connection to a propylene container. An excess of propylene was distilled off from the container to the cylinder by cooling the cylinder down to –85°C, using an alcohol slush bath. The cylinder was detached from the propylene container and the correct monomer ratio obtained by flushing off the excess propylene. The cylinder was then attached to the autoclave and nitrogen bottle.

Prior to the polymerisation reactions the jacket temperature was set at 80°C, the reactor evacuated for 30 min and subsequently refilled with UHP nitrogen. This procedure was repeated 4 times. The jacket temperature was then set to 20°C and the autoclave flushed with nitrogen for 20 min.

The solvent was introduced to the autoclave from a graduated Schlenck tube using cannula technique. The co-catalyst, transferred by a gas-tight syringe, was then added, followed by the addition of the titanium catalyst. The catalyst system was aged for 15 min before introduction of the monomer mixture. The autoclave was subsequently pressurised via the monomer cylinder from the attached nitrogen bottle.

To control the propylene / 1-hexene comonomer ratio within the reactor, the propylene was liquefied [3]. This was accomplished by performing the copolymerisation reactions at a temperature of 20°C and a pressure of 1,4 MPa (14 bar). The vapour pressure of propylene at 20°C is about 1 MPa (10 bar).

After 40 min the autoclave was depressurised, the reaction terminated and the copolymer precipitated by the addition of 100ml methanol.
The polymer product was removed via the valve at the base of the autoclave. The copolymer was thoroughly washed consecutively with HCl/methanol mix, water, methanol and acetone before drying under vacuum.

The experimental parameters used in this study are given below:

Table 4.2: Experimental parameters used in the preparation of various propylene random copolymers with 1-hexene and 1-pentene

Experiment No.	Propene (mole)	1-Hexene (mole)	1-Pentene (mole)	X_C = C/P (Monomer Ratio)	Reaction conditions
PP co Hex 1	0,6825	0,6825	0	1	12 bar/25°C
PP co Hex 2	0,6825	0,6825	0	1	14 bar/20°C
PP co Hex 3	1,092	0,273	0	0,25	14 bar/20°C
Pp co Hex 4	1,187	0,178	0	0,15	14 bar/20°C
PP co Hex 5	1,56	0,624	0	0,4	14 bar/20°C
PP co Hex 6	1,365	0,819	0	0,6	14 bar/20°C
PP co Hex 7	9,5057	1,90114	0	0,2	14 bar/20°C
PP co Hex 8	10,2026	2,0405	0	0,2	7 bar/25°C
PP co Pent 1	11,8818	0	2,1387	0,18	14 bar/20°C
PP	10, 7581	0	0	-	7,88bar/?25°C

- Et_2 AlCl (DEAC) and $TiCl_3$ 0,33 $AlCl_3$ catalyst system used throughout
- Monomer/solvent molar ratio fixed at 0,4
- 500ml Heptane used as solvent for each preparation.
- Catalyst/Total monomer molar ratio fixed at $2,5 \times 10^{-3}$
- Al to Ti ratio fixed at 3.

4.2.3 Polymer analysis

4.2.3.1 ^{1}H NMR

According to Xu et. al. and Piloz et. al. [4, 5] it is possible to analyse the propylene / α-olefin copolymer composition using ^{1}H NMR. Kissin et. al. and others [6,7] also describe the analysis of copolymer composition by ^{13}C NM. According to Pilotz et. al. the methyl protons ($-CH_3$) are suitably separated from the methylene ($-CH_2$) and methine (-CH) protons which practically overlap each other.

By naming the area of the methylene / methine and methyl protons 'A' and 'B' respectively, he derived the relevant formulas to calculate the propylene and 1-hexene fractions present in propylene / 1-hexene random copolymers, namely:

$$\text{Propylene fraction} = \frac{3B - A}{2B}$$

$$\text{Hexene fraction} = \frac{A - B}{2B}$$

Using the same philosophy the author developed formulas to calculate the propylene and 1-pentene fractions present in propylene / 1-pentene random copolymers, namely:

$$\text{Propylene fraction} = \frac{7B - 3A}{4B}$$

$$\text{Pentene fraction} = \frac{3A - 3B}{4B}$$

Solutions of copolymers in the 2 to 3% (3mg in 0,8ml) concentration range were prepared in deuterated 1,1,2,2-tetrachloroethane. The solution was heated to approximately 140°C to dissolve the copolymer completely. The average copolymer composition was determined utilising a high-resolution 200 MHz Varion ^{1}H NMR spectrometer. The sample spectra were recorded at a temperature of 140°C with a 30 second delay time and a 80° pulse using 5mm probes.

At 200 MHz frequency the resonance of the methyl protons is well separated from the methylene and methine protons for both the propylene / 1-hexene and propylene / 1-pentene random copolymers as shown in the table below.

Table 4.3: Frequency ranges of the methyl proton resonances

Random Copolymer	**Resonance Range**	
	Methyl Protons	**Methylene and Methine Protons**
Propylene / 1-Hexene	0,62 – 1,07	1,1 – 1,9
Propylene / 1-Pentene	0,62 – 1,07	1,1 – 1,9

4.2.3.2 Thermal analysis

DSC was carried out on a Perkin Elmer DSC-7 instrument. The propylene homopolymer and random copolymer samples were pre-heated to 200°C at a rate of 50°C/min, held at that temp for 5 min and cooled to 20°C. The samples were subsequently analysed under a nitrogen atmosphere at a scanning rate of 20°C/min.

4.2.3.3 Light microscopy

A Leitz Laborlux-s microscope equipped with a thermostatically controlled hot stage was used to determine spherulite size. The microscope is fitted with a polarising filter and a 35mm camera with a light intensity meter automatically controlling the exposure time. The respective random copolymers were

melted on the hot-stage where after thin films were passed between the two glass plates. The films were subsequently allowed to cool to room temp (on the hot stage) and photos taken.

4.2.3.4 Wide Angle X-Ray Diffraction (WAXD)

X-ray determination of crystallinity in PP is a well-researched field [8,9,10]. A two-phase model was used for determining the crystallinity of PP. In this model it is assumed that a polymer has both a crystalline phase and a non-crystalline (amorphous) phase. When x-rayed, the crystalline phase gives diffraction effects, which is observed as peaks in the diffractogram. The non-crystalline phase results in the dispersion of x-rays – so that only the amorphous "halo' of the dispersed x-rays are observed. The degree of crystallinity is obtained from the relationship between the crystalline peaks and the amorphous " halo". It can be done after the background, as a result of for example light scattering and electronic and thermal noise has been subtracted. The two phases are evident from the diffractograms shown in Figure 4.5.

It should be mentioned that the two-phase concept is rather old and has some shortcomings. One very important one is the fact that crystal defects also contribute to the amorphous 'halo' and not to the crystalline peak. The degree of crystallinity is therefore lower than it should be. The advantage however is that it has the possibilities of routine determinations, especially in cases where the relative values are more important than the absolute values. According to the literature, the two-phase concept is an acceptable approach if the crystallinity is less than about 50%.

A procedure proposed by Natta and coworkers [9] was used for the construction of the background. The basic point in their procedure assumes that the height of the maximum of the background corresponds to that of the minimum between the two 110 and 040 crystalline peaks that occur at 2θ = 14,0° and 17,0° respectively. In addition the maximum of the background is taken to lie at the same angle of diffraction (2θ = 16.3°) as in the diffraction curve of an entirely amorphous sample. The background curve constructed mirrored the diffraction curve of a totally amorphous sample.

The degree of crystallinity is obtained from the areas in the represented diffractograms, by determining the crystalline and amorphous phases. The crystallinity is obtained from:

$$X_c = \frac{A\,I_{110} + B\,I_{040} + C\,I_{130} + D\,(I_{111} + I_{13\text{-}1} + I_{041})}{A\,I_{110} + B\,I_{040} + C\,I_{130} + D\,(I_{111} + I_{13\text{-}1} + I_{041}) + E\,I_a}$$

where:

I_{hk1}: Intensity of the crystalline peak of PP.
hk1 indicates the Miller symbols of the crystalline peaks.

I_a: Intensity of the amorphous 'halo'.

The constants A to E are weighted factors, to make provision for the Lorentz and polarisation factors [8] as well as the absorption and a geometric factors. The given values for the constants used are listed below.

A	1.00
B	1.69
C	2.25
D	3.37
E	0.90

4.3 RESULTS AND DISCUSSION

4.3.1 Copolymer composition

The copolymer composition is different from that of the initial comonomer ratio in the reaction medium. This is due to the different reactivity ratios of the respective monomers. This phenomenon also results in a drift in comonomer composition with time during the copolymerisation reaction. The drift in the comonomer ratio is however strongly dependent on the conversion and thus on the duration of the copolymerisation reaction. Below 20% conversion the drift in copolymer composition is relatively small. The average conversion of the copolymerisation reactions was therefore kept below 20%.

Pilotz et al [5] published a set of reactivity ratios for the copolymerisation of 1-hexene (0,16) and propylene (4,18) as determined by the linearisation method (Fineman-Ross plot) [11, 12]. Applying these values to the copolymerisation equation as proposed by Alfrey and Goldfinger [13], a prediction with regard to the copolymer composition for specific monomer ratios was made. The equation for the propylene/1-hexene copolymerisation can be written as follows:

$$\frac{m_{prop}}{m_{hex}} = \frac{M_{prop}}{M_{hex}} \times \frac{r_{prop} M_{prop} + M_{hex}}{r_{hex} M_{hex} + M_{prop}}$$

where:

r	reactivity ratios
m	mole percentage of monomer present in the copolymer
M	molar concentration of monomer in solution.

The average copolymer composition was determined by 1H NMR as described in Section 4.2.3.1 and compared with the predicted values. Table 4.4 shows that there is a good correlation between predicted and calculated (NMR) values. The low average conversion rate at which the reactions were terminated resulted in a very uniform random copolymer.

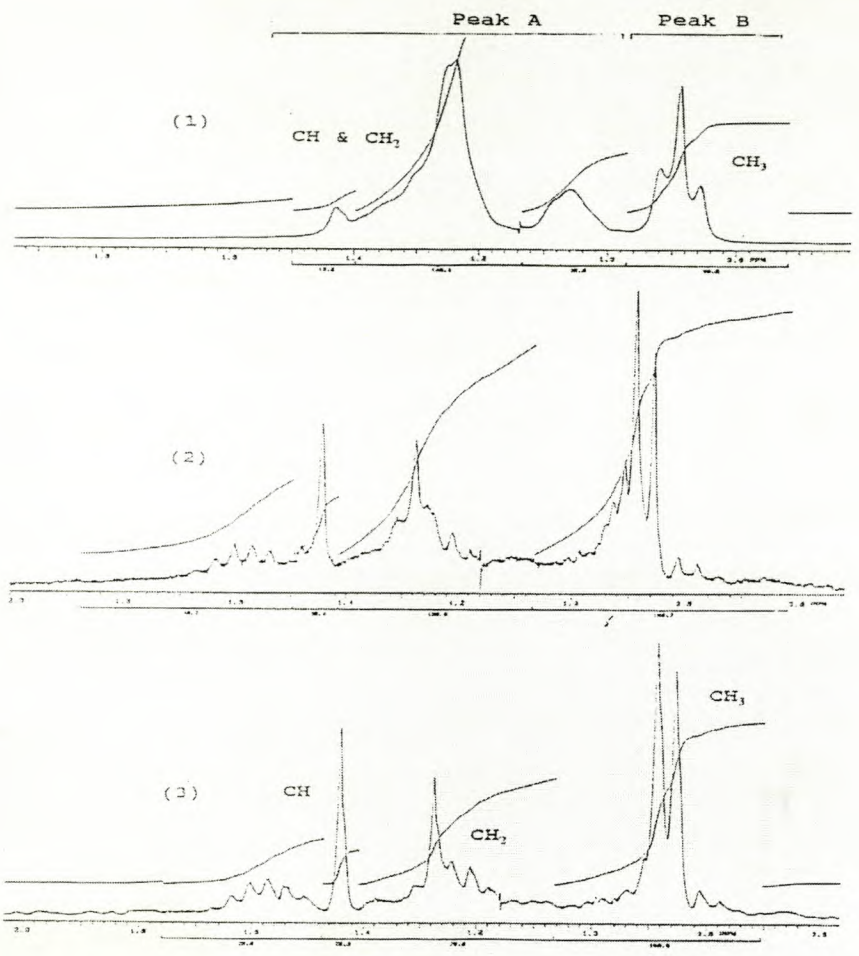

Fig 4.1: 1H NMR spectra of (1) poly (1-hexene) and (2 – 3) PP / 1-hexene copolymers with 20% and 7% 1-hexene content, respectively.

Table 4.4: Copolymer composition predicted and calculated from NMR analysis.

Experiment Nr	Xc=1-Hex/Prop	Comonomer content (predicted)	Comonomer content (from NMR)	Conversion %
PP co Hex 1	1	18	16,26	10,2
PP co Hex 2	1	18	19,98	15,1
PP co Hex 3	0,25	5,5	6,67	13,0
PP co Hex 4	0,15	5,5	4,82	12,9
PP co Hex 5	0,4	8,5	n.d.	15,5
PP co Hex 6	0,6	12,1	n.d.	11,7
PP co Hex 7	0,2	4,6	n.d.	12,6
PP co Pen 1	0,18	4,1	4,7	13,8
PP	0	0	0	19,3

4.3.2 Thermal analysis

The information gathered from the DSC thermograms in Fig 4.3 are summarised in Table 4.5.

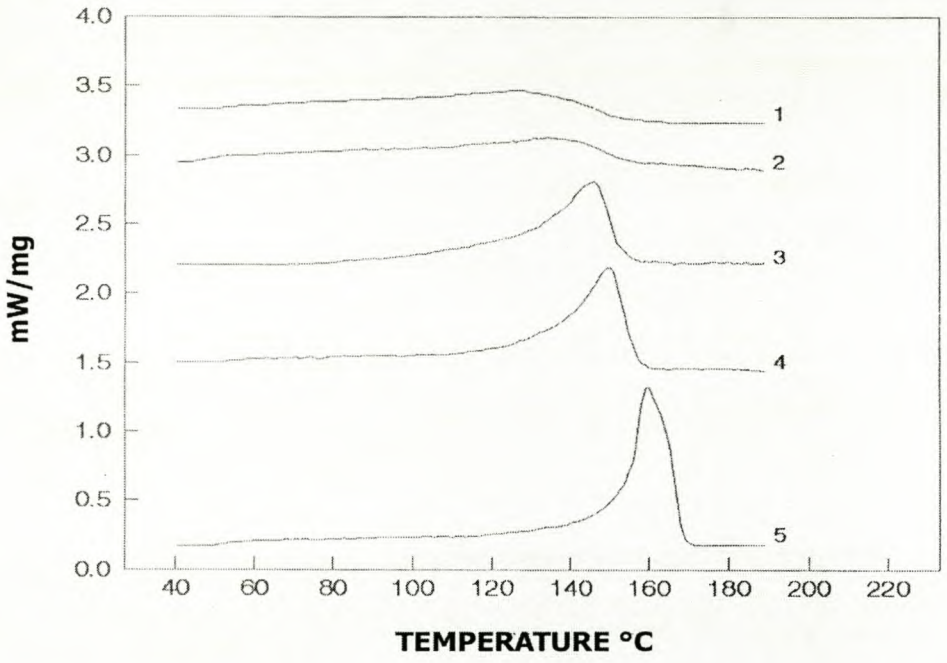

Fig 4.2: DSC plots of (1-4) propylene /1-hexene random copolymers with 16, 20, 7 and 4 % hexene content respectively and (5) PP.

Table 4.5: Thermal properties of propylene homo- and random copolymers

Experiment Nr.	Comonomer content (NMR)	Melting point (°C) **	Heat of fusion (J/g)	Relative crystallinity***
PP co Hex 1	16,3	138,9	31,90	0,32
Pp co Hex 2	20,0	131,8	26,07	0,26
PP co Hex 3	6,7	146,6	72,60	0,73
PP co Hex 4	4,82	150,3	81,22	0,82
PP co Hex 5	8,5*	141,5	58,02	0,59
PP co Hex 6	12,1*	136,2	49,47	0,50
PP co Hex 7	4,6*	145,1	70,25	0,71
PP co Pen 1	4,7	145,2	74,11	0,75
PP	0	161,0	98,91	1

* Predicted value (Alfrey and Goldfinger)
** Peak melting point (determined from DSC curves)
*** The fusion enthalpy (Joule/gram) of the copolymers produced compared to that of PP (taken as unity)

Geometrical regularity and packing efficiency of the molecular structure are general requirements for crystallisation. Isotactic PP, due to its geometrical regularity, exhibits highly crystalline behaviour. The random incorporation of 1-hexene into the backbone disrupted the packing efficiency thereby decreasing the relative crystallinity and depressing the melting point.

4.3.3 Light microscopy

Bulk crystallised polymer consists essentially of spherulites. Polypropylene melts have a high crystal growth rate and tend to form coarse-grain superstructures (spherulites) while processed. This results in coarse structures that adversely affect the transparency of the PP article [14]. 1-Hexene articles appear to supercool [15] to a significantly higher degree than PP homopolymers and ethylene copolymers at fast cooling rates (for commercial purposes the cooling rate is very rapid) and as such promotes the formation of much finer spherultic structure [16]. This leads to some distinct property advantages, such as improved clarity and impact strength.

The finer spherulitic structure of the 1-hexene copolymers is clearly evident from Figure 4.4. It should be considered that on account of its semi-crystalline structure PP copolymers cannot fully attain the optical properties of amorphous materials. Within the group of polyolefins however its transparency can be called very good. In addition PP has good contact clarity and moulds with high surface-finish can further improve the clarity of the end product.

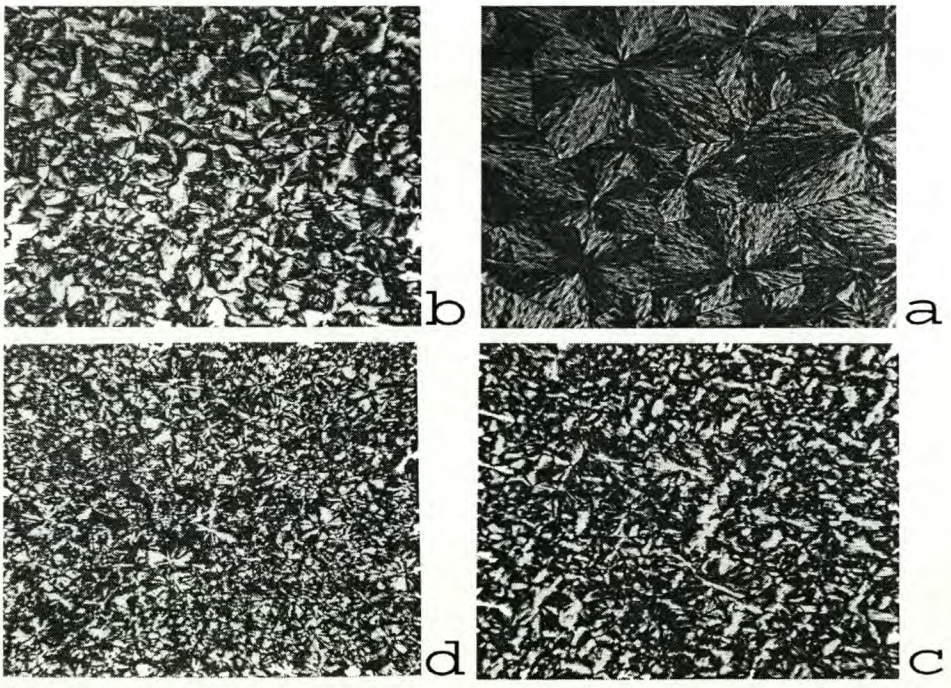

Fig. 4.3: Finer spherulite structures of PP homopolymer (a) and 1-hexene random copolymers with 1wt% (b), 4 wt% (c)and 7 wt% (d) comonomer content respectively as seen under a polarising light microscope.

4.3.4 Crystallinity

Determinations were done in four-fold, on the same diffractogram, and the results obtained are shown in Table 4.6.

Table 4.6: Results from WAXD crystallinity determinations

Sample No.	Crystallinity (%)	Standard deviation (%)
PP (0% hexene)	51,4	0,8
PP co Hex 4 (4% 1-hex)	39,6	0,5
PP co Hex 3 (7% 1-hex)	40,5	1,3
PP co Hex 5 (9% 1-hex)	39,6	0,7
PP co Hex 6 (13% 1-hex)	38,4	1,3
PP co Hex 1 (17% 1-hex)	37,8	1,2
PP co Hex 2 (20% 1-hex)	36,5	1,3

On taking the standard deviations into consideration, it appears as if the samples with respectively 4, 7and 9% 1-hexene content do not differ significantly. Similarly, the samples with 13 and 17% 1-hexene content do not differ much. It appears that the orientation and especially the position of the 1-hexene side chain in the propylene chain has a greater disturbance on the crystal than the amount of 1-hexene. There is a general decrease in the degree of crystallinity as the amount of 1-hexene increases.

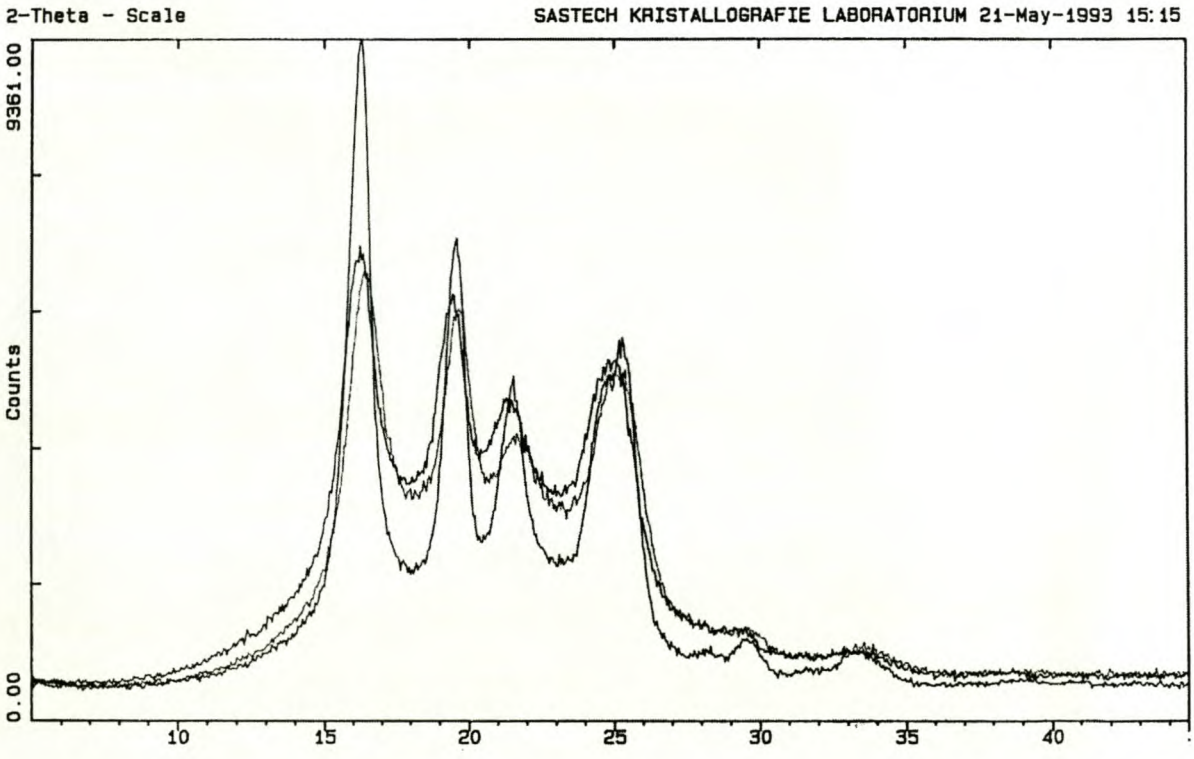

Fig 4.4: X-ray Diffraction Patterns

It is also noticed that there is an additional peak at 12 °2Φ in the diffractograms of the samples with respectively 17 and 20% 1-hexene content. This peak is probably a result of order that arises as a result of the high hexene content. This peak was included in the amorphous 'halo' and not under the crystalline peak in the calculation.

4.4 CONCLUSIONS

A range of propylene / 1-hexene and 1-pentene random copolymers with different comonomer contents was successfully prepared in slurry-phase with a controlled initial comonomer content. This was done in a 1-l autoclave, using the second generation $TiCl_3 0{,}33AlCl_3$-Et_2AlCl catalyst system.

An innovative way of controlling the co-monomer ratio within the reactor was developed. This was accomplished by conduction of the polymerisation reaction at pressures exceeding the vapour pressure of propylene. To avoid heterogeneity in the composition of the copolymers the average conversion of the copolymer reactions was kept below 20% (20% monomer was incorporated into the backbone).

Copolymer compositions were determined by 1H NMR spectroscopy and the results correlated well with the theoretical values obtained by applying a set of published reactivity constants to the copolymerisation equation.

The reduction in crystallinity and the depression of the melting point with increasing comonomer content were studied by DSC. To compliment this, the effect of incorporating 1-hexene and 1-pentene into the polymer backbone on the crystal structure of the polymer, was investigated by light microscopy. The random copolymers exhibited a finer spherulitic structure. This is because of the significantly higher degree of supercooling compared to that of PP homopolymers and is responsible for the improved clarity and impact strength of these polymers.

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CHAPTER 5

PREPARATION AND CHARATERISATION OF RANDOM COPOLYMERS OF PROPYLENE AND 1-PENTENE IN GAS-PHASE

5.1 INTRODUCTION

The positive results achieved during the random copolymerisation of propylene with 1-hexene and 1-pentene led to the decision to expand the investigation to the gas-phase preparation of these materials. Easy incorporation of the bulky 1-pentene and 1-hexene monomers into the propylene backbone, using a commercially available second generation Ziegler-Natta catalyst, in combination with the effective melting point depression and reduction in spherulite size, fuelled the interest in these random copolymers.

The advantages that gas-phase polymerisation units offer, over slurry and bulk processes, in the production of highly engineered propylene / α-olefin random copolymers is discussed here. To facilitate the production of these random copolymers in gas-phase it is a fundamental requirement that the gas mixture in the reactor, at the typical operating conditions, is well above its dew (condensation) point. Theoretical dew point simulations with both 1-pentene and 1-hexene as comonomer and at selected concentrations had therefore to be conducted.

A range of propylene / 1-pentene random copolymers was successfully produced in the gas-phase and characterised with regard to composition and crystal structure. With the advent of the introduction of fourth generation catalyst systems in most commercial production units it was later decided to prepare the copolymers using this state-of-the-art catalyst system.

Finally, a kinetic study was also conducted to evaluate the effect of introducing α-olefin to the propylene polymerisation process on the activity of the fourth generation catalyst.

5.2 GAS-PHASE VERSUS SLURRY AND BULK PROCESSES

The production processes currently used for the production of the PP family of products are as follows [1]:

- Slurry Polymerisation
- Bulk Polymerisation
- Gas-phase Polymerisation

According to Ficker et. al. [2] and Seiler et. al. [3] the production of random copolymers by bulk and slurry polymerisation technologies are limited by several process restrictions, such as:

- High solubility of random copolymer product in reaction medium
- Limitations on comonomer concentration in reactor
- Molecular weight control.

With increasing comonomer content the copolymer product, due to a reduction in crystallinity and melting point [4], becomes increasingly soluble in the hydrocarbon reaction medium of the slurry (hexane) and bulk (liquefied propylene) polymerisation processes. This results in an increase in the viscosity of the production medium, fouling and eventual shutdown of the reactor. As such the slurry and bulk polymerisation processes are limited to approximately 4% ethylene incorporation compared to the 10 – 12% incorporation obtained with the gas-phase polymerisation process.

Higher α-olefins react more slowly than propylene does and therefore higher concentrations are required in the liquid medium [5, 6]. This creates yet another problem, especially for slurry processes, as separation from the reaction medium becomes progressively more difficult with increasing comonomer content, subsequently requiring a larger capital investment.

Hydrogen is universally used as chain transfer agent in the manufacturing of PP products [7, 8, 9]. Under normal operating conditions in bulk and slurry polymerisation processes hydrogen does not condense. The ability to produce ultra high melt-flow products is thus limited by the capability to dissolve sufficient hydrogen in the reaction medium. No such limitations apply to the gas-phase polymerisation processes.

The production of high ethylene-content, random PP copolymers by the gas-phase processes do nonetheless have limitations. The heat of evaporation of the recycled comonomer stream in the gas-phase processes is used to control the temperature of the exothermic reaction process. Ethylene, in addition to the fact that it has a higher heat of reaction, does not condense during the recycle process and as such does not contribute much to the heat removal process.

The use of higher α-olefins in the production of PP random copolymers has the opposite effect and the heat of evaporation is directly related to the molecular weight of the monomer. However, there are also limitations to the use of higher α-olefins in the gas-phase production of random PP copolymers, as condensation of the heavier monomers is not permitted.

5.3 DEW POINT CALCULATIONS

5.3.1 Introduction

Prior to carrying out these copolymerisation reactions, as mentioned in the paragraph above, it had to be determined whether 1-pentene or 1-hexene would remain in the gas phase. Hence the dew points of selected gas mixtures of propylene, selected comonomers and hydrogen were calculated. These calculated dew points were then compared to typical operating conditions for

gas-phase production units to establish the feasibility of utilising higher α-olefins in the production of PP random copolymers.

5.3.2 Experimental

The dew points of selected mixtures of hydrogen, 1-pentene or 1-hexene and propylene were calculated to determine feasible operating conditions for the preparation of random copolymers. Literature [7, 8, 9] suggested a hydrogen / propylene molar ratio in the range of 0.001 to 0.2, a 1-hexene or 1-pentene / propylene molar ratio of 0.04 to 0.08, operating pressures between 17 and 35 bar and operating temperatures between 60 and 90°C.

Flash calculations were done with the Pro/II software package, using the NRTL thermodynamic option, to estimate dew point temperatures. The pressure / dew point correlation approached linearity in the range that was selected.

5.3.3 Results and Discussion

The following relationships emerged from the simulations:

- The dew point increases with pressure for a specific gas composition.
- There is an indirect relationship between the hydrogen / propylene molar ratio, at a specific pressure and comonomer ratio, and the dew point.
- There is a direct relationship between 1-pentene / propylene molar ratio, at a specific pressure and hydrogen / propylene molar ratio, and the dew point.

The results from the computer simulations are presented in Tables 5.1 and 5.2.

Table 5.1: Dew points of selected 1-pentene mixtures

Pressure (bar)	H_2 (mole)	1-pentene (mole)	Propylene (mole)	Dew point (°C)
17	1	8	100	63.8
35	1	8	100	98.3
17	1	4	100	54.8
35	1	4	100	79.1
17	0.1	8	100	64.2
35	0.1	8	100	98.7
17	0.1	4	100	55.1
35	0.1	4	100	89.5
17	10	8	100	60.6
35	10	8	100	94.6
17	10	4	100	51.4
35	10	4	100	85.3

Table 5.2: Dew points of selected 1-hexene mixtures

Pressure (bar)	H_2 (mole)	1-hexene (mole)	Propylene (mole)	Dew point (°C)
17	1	8	100	86.3
35	1	8	100	120.0
17	1	4	100	71.7
35	1	4	100	104.4
17	0.1	8	100	86.6
35	0.1	8	100	118.9
17	0.1	4	100	72.2
35	0.1	4	100	103.3
17	10	8	100	83.2
35	10	8	100	116.3
17	10	4	100	68.5
35	10	4	100	100.7

5.3.4 Conclusions

The most productive temperature range for a typical fourth generation catalyst system is between 70 and 85°C [9]. There is also a direct relationship between pressure and polymerisation rate [9, 10]. The typical operating conditions for the production of ethylene / propylene random copolymers are a temperature and pressure of 80°C and 17 bar respectively. As there is normally a temperature gradient within the reactor it is of critical importance to operate at conditions well above the dew point of the gas mixture in the reactor in order to prevent condensation from taking place.

The effect of variation in the hydrogen / propylene molar ratio in the reactor gas mixture is relatively small, with a 100-fold increase resulting in a ca. 4°C decrease in dew point temperature. In comparison, a 100-fold increase in the 1-pentene (1-hexene) / propylene molar ratio results in about a 10-15°C increase in dew point temperature. Increasing the reactor pressure from 17 bar to 35 bar for a specific gas composition leads to a dew point increase of about 35°C.

Mixtures should be chosen to assure gas phase operation and required end-product properties. Taking all of this into account it became clear that use of 1-hexene as a comonomer for the production of PP random copolymers on a commercial gas-phase plant was not feasible. However, from Figure 5.1 below, it is obvious that at a typical operating pressure of 17 bar, a low hydrogen-to-propylene ratio and a relatively high 1-pentene / propylene comonomer ratio of 8%, the calculated dew point of ca. 64°C is well below the operating temperature of 80°C in a typical reactor. Hence the focus of this research project shifted to the exclusive use of 1-pentene as potential comonomer in the production of PP random copolymers.

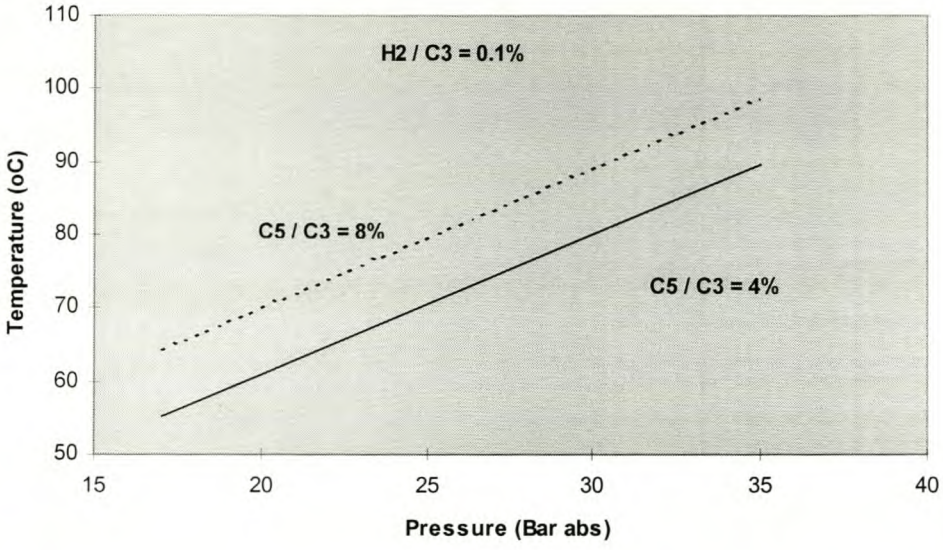

Figure 5.1: Dew Points of Selected C5 / C3 Mixtures (Molar Ratio)

5.4 EXPERIMENTAL

5.4.1 Polymerisation procedure for gas-phase copolymerisation reactions

The typical polymerisation method used for the gas-phase copolymerisation of propylene and 1-pentene, utilising a fourth generation Ziegler-Natta catalyst system, is summarised below [6, 9, 11]. These copolymerisation reactions were carried out in BASF's polymer laboratory in Ludwigshafen, Germany.

A small amount (about 50g) of homopolymer powder is transferred into the 10- litre autoclave under nitrogen counterflow. The stirrer is activated and the temperature inside the reactor adjusted to 40°C. This is followed by first the introduction of the aluminiumalkyl cocatalyst, then the silane external donor and finally the supported Ziegler-Natta catalyst. In the next step hydrogen is added to the reactor.

The temperature in the heating jacket is increased to achieve a polymerisation temperature of 80°C inside the reactor. The monomers are then introduced into the reactor at a selected molar ratio by progressively raising the pressure until a polymerisation pressure of 30 bar is reached. During the polymerisation process the reactor pressure is kept constant with a pressure regulator connected to a comonomer reservoir under high pressure.

Cooling down the reactor, closing off the comonomer feed and depressurising the reactor stopped the polymerisation process. The autoclave was subsequently pressurised with nitrogen (7 bar) followed by depressurisation.

This procedure was repeated three times before the polymer powder was discharged from the reactor.

The individual reaction conditions used in the gas-phase preparation of the 5 batches of propylene / 1-pentene random copolymers are listed below.

Al/Ti molar ratio:	220/1
Ti/propylene molar ratio:	1/200.000
Propylene/pentene-1 molar ratio:	170/1 in the case of C3/C5 Copol 1 82/1 in the case of C3/C5 Copol 2 42/1 in the case of C3/C5 Copol 3 28/1 in the case of C3/C5 Copol 4 7/1 in the case of C3/C5 Copol 5
H2/Ti molar ratio:	2800/1 in all cases.
Residence time:	10min to reach polymerisation conditions 90 min at polymerisation conditions in all cases except C3/C5 Copol 1, where polymerisation was stopped after 40 min.
Pressure:	30 bar in all cases.
Temperature:	80°C in all cases.
Stabilisation procedure:	Polymer powder and stabiliser were thoroughly mixed together by shaking in a plastic bag.
Deactivating procedure:	No deactivating procedure carried out.

The amount of initial homopolymer powder in the autoclave is very small compared to the total amount of PP random copolymer produced during the run; hence its influence is negligible.

5.4.2 Polymer analysis

5.4.2.1 Thermal analyses of propylene / 1-pentene random copolymers

The same analytical procedure as described in Section 4.2.3.2 was used to determine the melting behaviour of the random copolymers.

5.4.2.2 ^{1}NMR analysis of propylene / 1-pentene random copolymers

The same analytical procedure as described in Section 4.2.3.1 was used to determine the molecular composition of the random copolymers.

5.4.2.3 WAXD analysis propylene / 1-pentene random copolymers

The same basic procedure as described in Section 4.2.3.4 was used to determine the crystalline content of the random copolymers. However, in addition to determining the total crystalline content the random copolymers they were also analysed with regard to the different crystalline forms found in isotactic PP.

Various researchers have described the polymorphs of the monoclinic (α) -, the hexagonal (β) -, the triclinic (γ) – crystal forms and the smectic form [12, 13, 14].
The α-crystalline form is dominant in isotactic PP [15]. The content of the β- and γ -crystalline forms were measured relative to the dominant reflections of the α-crystalline form [16]. The different phase reflections for the respective crystalline forms are:

α1 - crystalline peak (110) at 2θ = 14,1°
α2 - crystalline peak (040) at 2θ = 16,9°
α3 - crystalline peak (130) at 2θ = 18,5°

β - crystalline peak (300) at 2θ = 16.1° [15, 17]

γ - crystalline peak (117) at 2θ = 20,05° [17, 18]

5.4.2.4 Infrared (IR) analysis of propylene / 1-pentene random copolymers

A practical IR method was developed for the determination of the 1-pentene content in the random copolymers. A calibration curve was obtained by plotting absorbance divided by film thickness against the concentration of poly(1-pentene) in melt blends of propylene with known poly(1-pentene) content. The melt blends were obtained by kneading the two polymers on a Brabender plasticorder at 230°C and then pressing a film from the blend.

The moderately strong peaks at 969 cm^{-1} in the spectrum of polypropylene arise from coupling vibrations and involves the coupling of the backbone C-C stretch with the CH_3 rocking mode [16, 19, 20]. The rocking of the CH_3 group is used to determine polymethylenic branching as low as C_2 to C_5. The 1-pentene peak is at 734 to 743 cm^{-1}. The results correlate well with ^1H NMR determinations in 1,2 dichlorobenzene.

A typical correlation, over a wide range of copolymer contents, between IR and ^1H NMR results, the calibration curve and a typical IR spectrum for a propylene / 1-pentene random copolymer are shown in Table 5.3, Figure 5.2 and 5.3.

Table 5.3: Comparison between IR and ^1H NMR copolymer content determinations

Sample	Calibration Curve		NMR (mass %)
	Conc. (total area) (mass %)	Conc. (peak height) (mass %)	
1	20.82	21.52	22.23
2	9.52	10.35	9.98
3	5.02	5.03	5.73
4	2.41	2.52	3.12

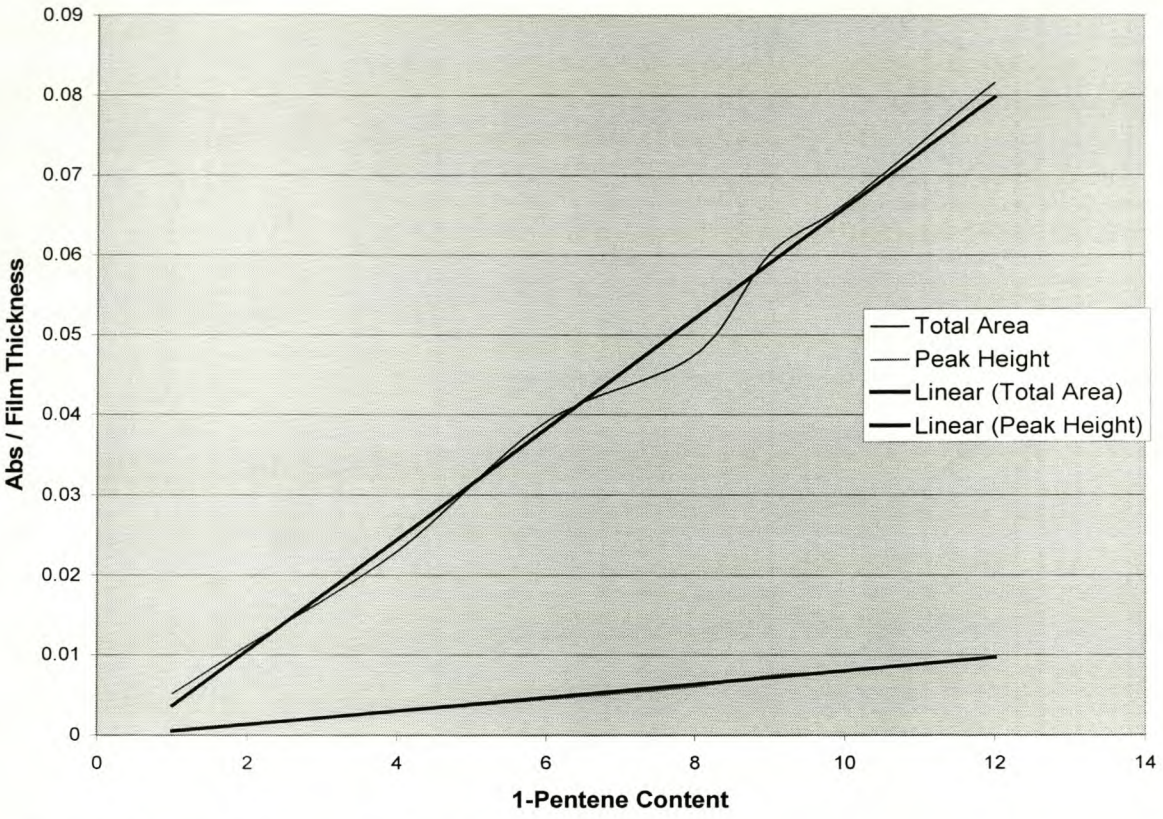

Figure 5.2: IR Calibration Curve

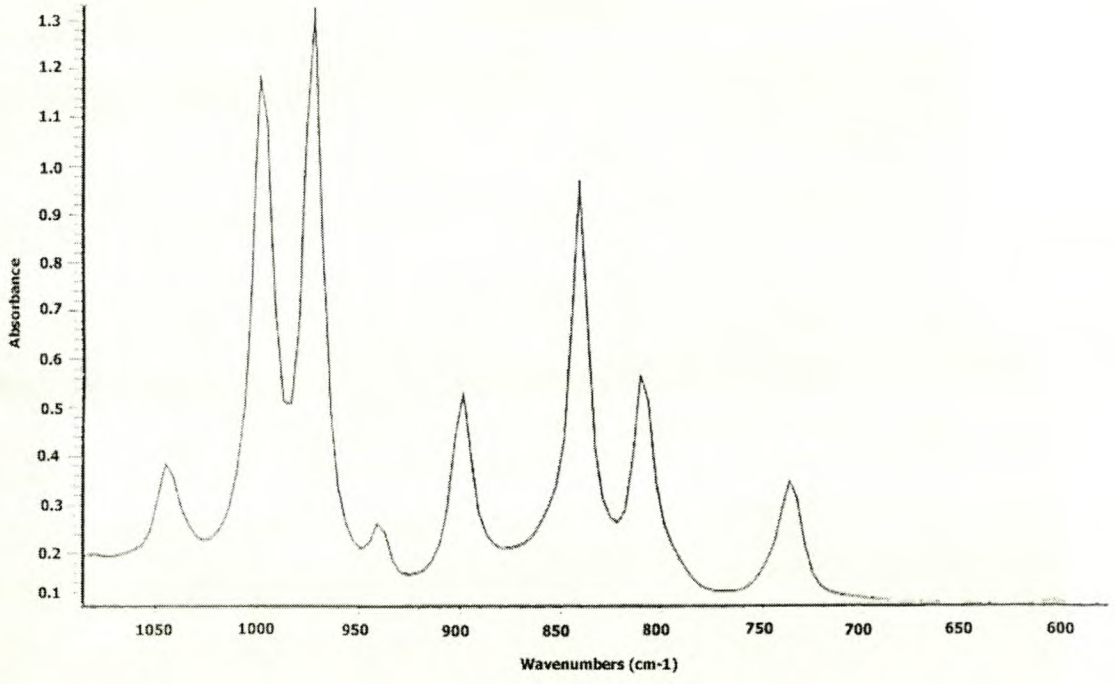

Figure 5.3: 1-Pentene Infrared Peak Assignment

5.4.2.5 Determination of solubles content in the random copolymers

For the determination of solubles content 5g of polymer is placed in a beaker filled with 500 ml of xylene. The mixture is boiled till all the polymer has dissolved. Dry ice is then used to cool mixture down to –5°C before it is slowly heated to 23°C. The polymer that has precipitated is weighed to determine the xylene solubles content expressed as a percentage.

5.5 RESULTS AND DISCUSSION

5.5.1 Random copolymer composition

The bulky 1-pentene comonomer was effectively incorporated into the polymer backbone during the gas-phase copolymerisation using a fourth generation supported Ziegler-Natta catalyst system. Good correlation was obtained between the ^{1}H NMR and IR analytical techniques used to determine the comonomer content in the random copolymer. The results are tabulated below.

Table 5.4: NMR and IR analysis of propylene / 1-pentene random copolymers

Sample	1-Pentene Content in Random Copolymers		
	IR Analysis (total area)	IR Analysis (peak height)	^{1}H NMR Analysis
C3/C5 Copol 1	1.03	0.92	1.12
C3/C5 Copol 2	1.97	1.67	2.09
C3/C5 Copol 3	3.11	2.96	3.04
C3/C5 Copol 4	4.04	3.81	4.21
C3/C5 Copol 5	5.86	5.42	5.56

5.5.2 Crystallinity of propylene / 1-pentene random copolymers

The propylene / 1-pentene random copolymers were also analysed with regard to their crystal structure using WAXD crystallography and compared to a typical PP homopolymer. The X-ray diffractograms show the presence of the α and the γ crystal forms, but there is no indication of the presence of the β crystal form. The primary effect of the 1-pentene comonomer present in the polymer backbone is to interrupt the isotactic and/or crystallisable sequences of the PP macromolecule, reducing overall crystallinity.

The formation of the γ crystal form has been observed for random copolymers with crystallisable propylene sequences and various copolymers [15, 21]. This observation would seem to suggest those short average lengths of isotactic sequences (high defect content) favour formation of the γ crystal form.

There is initially a 4% drop in the total crystallinity between the homopolymer and the random copolymer with the lowest comonomer content. Between samples with a 1,1% to 5,6% comonomer content there is little further

reduction in the overall crystallinity of the random copolymers. The results from the WAXD analysis is tabulated below and some diffractograms illustrated.

Table 5.5: WAXD analysis crystallinity and polymorphs in the propylene / 1-pentene random copolymers.

Sample	Comonomer (% pentene)	W ct (%)	W cα (%)	W c_γ (%)	W $c\alpha_2$ (nm)
Homo-PP	-	56	52	4	20,2
C3/C5 Copol 1	1.1	52	36	16	19.0
C3/C5 Copol 2	2.1	52	35	17	18.3
C3/C5 Copol 3	3.0	51	34	17	19.2
C3/C5 Copol 4	4.2	50	33	17	17.6
C3/C5 Copol 5	5.6	50	35	15	16.3

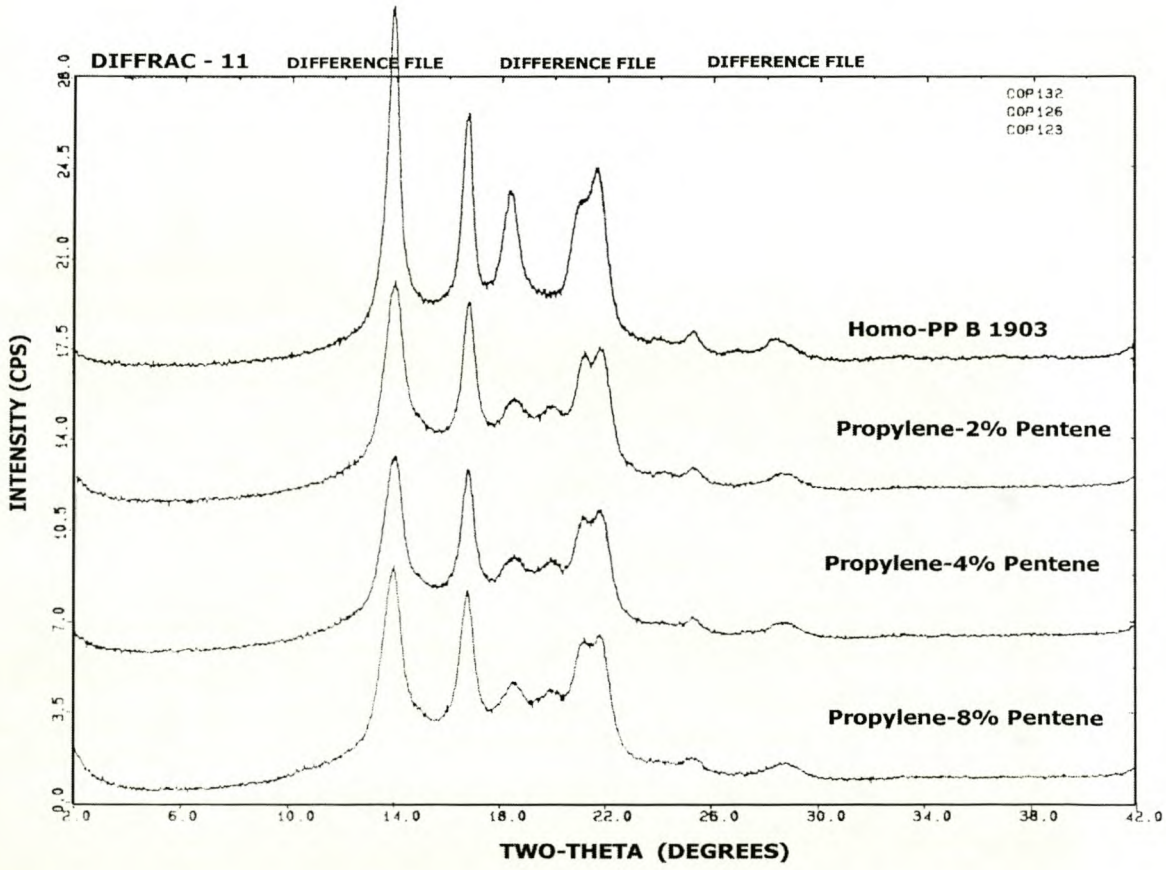

Figure 5.4: Diffractograms of PP homopolymer and a range of propylene / 1-pentene random copolymers

5.5.3 Thermal analysis of propylene / 1-pentene random copolymers

In Flory's theory of melting it is assumed that irregularities cannot be accommodated in the crystalline lattice and a lowering of the melting point was predicted with comonomer content [22]. In case of propylene disturbed by low levels of ethylene a decrease of 1,5°C per mole % of built-in ethylene was predicted. In practice the observed decrease was up to 5% [2]. When 1-butene was used as comonomer this effect was much lower [2, 23]. It was postulated that side groups larger than methyl are excluded from the propylene crystal [24]. The rate of onset melting temperature depression of propylene copolymers with 1-butene, 1-pentene and 1-hexene respectively is directly related to the molecular weight of the comonomer as well as the molar comonomer content in the random copolymer [25]. However, for peak melting point temperatures the decrease is far less and, moreover, quickly levels off [26].

The tabulated results and some DSC heat-flow curves obtained from the thermal analysis of the propylene / 1-pentene random copolymers are shown below.

Table 5.6: DSC analyses of C3/C5 gas phase random polymers

Sample	DSC melt Range (°C)	Fusion enthalpy (J/g)	Peak Melting Point (°C)
C3/C5 Copol 1	100 – 170	98	161.8
C3/C5 Copol 2	92 – 165	94	157.2
C3/C5 Copol 3	74 – 162	92	153.2
C3/C5 Copol 4	99 – 173	94	152.1
C3/C5 Copol 5	87 - 173	87	150.1

From the results presented the relationship between peak melting point and comonomer content of the random copolymers is confirmed. The reduction of overall crystallinity, as measured by the heat of fusion, supports the results obtained by WAXD analysis. From the heat-flow curves, shown below, it is evident that although there is a steady reduction in peak melting temperature, the width of the melting range increases dramatically with a corresponding increase in comonomer content. According to Hingmann and co-workers, this broadening of the melting range is due to a distribution of the thickness of crystalline lamella [27].

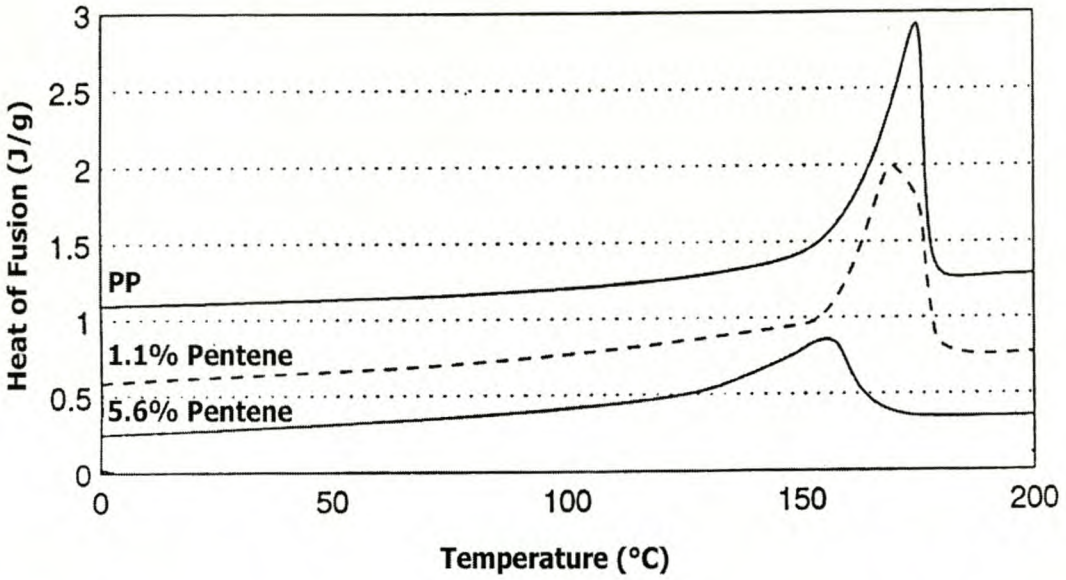

Figure 5.5: DSC heat-flow curves of PP homopolymer and propylene / 1-pentene random copolymers with 1.1 and 5.6% pentene content respectively.

Msuya and Yue also studied the correlation between the lamella thickness and the degree of crystallinity in semi-crystalline polymers [28]. They suggested that the dispersity of lamellae thickness can be represented by the formula $\Delta T = T_p - T_o$, where T_p is the peak melting temperature corresponding to the melting of crystallites with maximum lamellae thickness, and T_o is the onset temperature. They found that a linear relationship exists between the dispersity of lamellae thickness (ΔT) and the degree of crystallinity, but no relationship between maximum lamellae thickness (T_p) and crystallinity.

5.5.4 Xylene solubles of propylene / 1-pentene random copolymers

The use of PP random copolymers in the food and pharmaceuticals sectors is restricted by the solvent extractable fraction [3]. Ficker and Walker have reported a reduction in the solubles content of propylene / 1-butene random copolymers compared to ethylene copolymers with similar melting points [2]. It has been postulated by Galli and co-workers that the lower stereospecific catalyst sites are more reactive towards ethylene than 1-butene resulting in the production of less non-crystalline material [29]. This benefit is claimed in some PP random copolymer patents [30, 31].

The direct relationship between comonomer content and solubles content in propylene / ethylene random copolymers is not observed with the 1-pentene copolymers synthesised. The xylene solubles of the propylene / 1-pentene random copolymers analysed was in the range of 1,2 – 1,5%. This is superior to the xylene solubles content of commercially available propylene / ethylene random copolymers, with a 3% comonomer content, which is in the order of 8% [2]. The results are tabulated below.

Table 5.7: Xylene solubles and other properties of synthesised random copolymers

Sample	MFR (g/10')	C5 (m/m)	R 2/1*	Recryst-allisation (°C)	Xylene solubles (%)	Residu after Deashing (%)
C3/C5 Copol 1	6.3	1.03	11,5	119.3	1.5	0.06
C3/C5 Copol 2	6.7	1,87	13,4	117.3	1.1	0.06
C3/C5 Copol 3	8.1	3.11	15.0	115.3	1.3	0.06
C3/C5 Copol 4	7.6	4.04	16.1	114.6	1.2	0.07
C3/C5 Copol 5	10.0	5.86	20.0	112.5	Nd	0.40

* ^{13}C NMR measure of atactic content used by operators

5.6 CONCLUSIONS

Computer simulations of the dew points of selected gas mixtures indicated that 1-pentene can be safely introduced as comonomer for the production of random copolymers at normal operating conditions of commercial PP plants, without the danger of condensation occurring. The benefits of gas-phase processes over bulk and slurry technologies in the production of random copolymers were discussed.

A range of propylene / 1-pentene random copolymers was successfully synthesised in the gas-phase using a fourth generation Ziegler-Natta catalyst system. The copolymers exhibit a wide melting range indicating a wide distribution in the crystalline lamella thickness. The low extractable content of the propylene / 1-pentene random copolymers produced can be attributed to the low reactivity of 1-pentene towards non-stereospecific catalyst sites in relation to that of ethylene.

Methods to determine the comonomer content using the ^{1}H NMR and IR analytical techniques were developed and good correlation between them obtained. The relevant crystalline peaks in the WAXD diffractograms, for the 3 polymorphs present in PP polymers, were identified to support the characterisation of the random copolymer's crystalline structure.

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CHAPTER 6

MATERIALS AND METHODS USED IN THE DETERMINATION OF RHEOLOGICAL, THERMAL, CRYSTALLISATION, PHYSICAL AND MECHANICAL PROPERTIES OF SOME PROPYLENE / A-OLEFIN RANDOM COPOLYMERS ARE DESCRIBED.

6.1 INTRODUCTION

The NTH gas-phase polypropylene plant owned and operated by Sasol Polymers is well equipped for the production of propylene random copolymers [1]. The presence of higher α-olefins in Sasol's hydrocarbon stream and the ability to extract and purify these monomers to polymerisation grade requirements at a very competitive base cost (fuel alternative value plus purification cost), gives Sasol Polymers a competitive advantage in the production of propylene / higher α-olefin random copolymers. The successful laboratory synthesis of propylene / 1-pentene random copolymers in the gas-phase, using a typical commercially available catalyst system, and the interesting properties exhibited from the limited tests performed led to the decision to conduct an extensive study to fully characterise this new exciting family of propylene polymers.

A series of random propylene/1-pentene copolymers, propylene homopolymers and propylene/ethylene copolymers were prepared. The method of preparation of the materials is described in this chapter and the samples characterised with regard to their comonomer content as well as molecular weight and distribution. In Chapters 7, 8 and 9 the following properties of the random propylene/1-pentene copolymers are determined and compared with the properties of PP homopolymers and ethylene-containing copolymers:

- rheological properties (steady state and dynamic shear viscosity, creep compliance and plateau modulus),
- crystallisation properties (degree of crystallisation, modifications, kinetics of crystallisation),
- thermal properties (glass transition temperature, melting temperature, heat of fusion), and
- physical and mechanical properties (tensile strength, yield value, elongation, tensile modulus, impact strength, density, transparency etc.).

The effects of comonomer content, molecular mass and temperature were also investigated.

During the preparation of the series of propylene / 1-pentene random copolymers a kinetic study was conducted to evaluate the effect of comonomer content on the activity profile of the fourth generation supported Ziegler-Natta catalyst system.

6.2 POLYMERISATION

6.2.1 Materials

All solvents were obtained from Schümann-Sasol and purified by passing over 13X molecular sieves followed by Alcoa Selecsorb CD to remove moisture and oxygenated compounds to levels below 5 ppm.

The α-Olefins were obtained from Sasol's Fischer Tropsch process and purified by passing over 13X molecular sieves followed by Alcoa Selexsorb CD to remove moisture and oxygenated compounds to levels below 5 ppm.

Ethylene was obtained from Fedgas and Propylene from Sasol Polymers' PP plant. The monomers were purified by passing through a 1,8 m column with inside diameter of 20 mm and containing 13X molecular sieves and Alcoa Selexsorb CD in a 50:50 ratio.

Di-*iso*-propyl dimethoxy silane was also obtained from Sasol Polymers' PP plant and degassed before use.

Aluminium alkyls were obtained from Ethyl Corp., Akzo and Witco and diluted as required.

High purity nitrogen and hydrogen were obtained from Fedgas and used after passing through Messer Griesheim Oxisorb columns.

A fourth generation Ziegler-Natta catalyst system, supported on $MgCl_2$, was obtained from Sasol Polymers' plant and used as received.

The polypropylene homopolymers were of the Sasol 1101 type produced on a $50m^3$ Novolen gas-phase plant using the same catalyst system mentioned above [2]. Homopolymers with a range of different average molecular masses were selected.

Copolymers were prepared in heptane slurry or gas-phase, using the $MgCl_2$ supported Ziegler-Natta catalyst system, at temperatures of between 20 and 85 ^{0}C at pressures between 6 and 30 bar.

6.2.2 Polymerisation equipment

A Büchi BEP 280 reactor system was used for all polymerisation reactions. The polymerisation system that was developed at Sasol facilitated both gas-phase and slurry polymerisations. The system is in many ways similar to the design of the stirred bed copolymerisation reactor that was developed at the Department of Chemical Engineering at the University of Wisconsin [3]. A computerised reactor control system, utilising Turbolink software, was developed. This system allowed the independent and controlled introduction of all monomers, solvents, hydrogen and nitrogen. Micro Motion flow meters, in tandem with Badger control valves, were used for the controlled introduction of propylene and solvent. Ethylene and hydrogen flows were

measured and controlled by Brooks flow controllers. Liqui flow controllers regulated the introduction of the pentene-1 comonomer.

The reactor is also equipped with an inlet for catalyst introduction, a vacuum line and stirring facility. A bursting disc and pre-set temperature and pressure limit controls were fitted to the reactor for safety reasons. This allows for the automatic venting of the reactor should overpressure or thermal runaway occur.

The reactor is fitted with two independent temperature sensors respectively giving feedback to the temperature and reactor control systems. The reactor temperature is controlled by a Julabo ATS3 control system by the circulation of respectively heating and cooling fluids through the reactor mantle.

Reactor pressure is measured independently by respectively a mechanical dial gauge and an electronic pressure gauge feeding back to the reactor control unit. Pressure, temperature and all feed rates are displayed and captured in real time by the control unit. The profile of pressure, temperature and feed rates against time can be displayed.

Slurry polymerisations were carried out in 1-, 5- and 10-litre Büchi reactors equipped with sight-glasses. The gas-phase polymerisations in 1-, 20- and 35-litre reactors have special stirrer configurations adhering to tight clearance specifications required for these reactions.

6.2.3 Polymerisation procedure

The polymerisation procedure followed was similar to the procedure described in Section 5.4.1 except that different comonomer feed ratios and hydrogen partial pressures were used to synthesise a range of copolymers with tailored molecular weight and distribution for the comparative study of rheological, thermal, mechanical and physical properties.

6.2.4 Kinetic study

The polymerisation procedure followed for the kinetic study was similar to the technique discussed in the paragraph above. The polymerisation rate under the selected set of conditions was determined by measuring the rate of monomer consumption at selected time intervals for the duration of the experiment. Similar procedures to perform polymerisation kinetic studies are described in literature [4, 5, 6, 7].

Listed in the table below are the relative flow rates of propylene and 1-pentene used in the kinetic study. A direct relationship between the respective monomer feed rates to the reactor and the resultant comonomer ratio in the random copolymer was established during the gas-phase synthesis of a range of propylene / 1-pentene random copolymers in Chapter 5. The shape of the curve depicting the influence of the relative 1-pentene flow rate on the catalyst activity is thus a good approximation of how a similar curve showing 1-pentene copolymer content vs. activity should look like.

Table 6.1: Relative flow rates of the respective monomers used in kinetic study

Experiment Number	Relative Propylene Flow Rate (g / minute)	Relative 1-Pentene Flow Rate (g / minute)
1	100	0
2	100	10
3	100	5
4	100	2,5
5	100	0
6	100	1,5
7	100	3,5

6.2.5 Polymer characterisation

The comonomer content was determined by a practical IR-method that was developed by Tincul and Potgieter and described in Section 5.4.2.4 [3].

The determination of molecular masses and distributions thereof was performed on a Waters 150CV GPC equipped with a computerised data acquisition system and a differential pressure and refractive index detector. Data handling was carried out using Viscotek 'trisec' version 3.0 software and Plgel 2 x mixed bed-B, 30 cm, 10 micron columns were used.

A single solution of each polymer sample was prepared by adding 15 ml of solvent (1,2-dichlorobenzene with anti-oxidant) to 30 mg of sample and boiling gently for twenty minutes to dissolve. Each solution was then filtered through a fibre pad at 140°C and part of each filtrate transferred to glass sample vials. The vials were then placed in a heated sample compartment and after an initial delay of thirty minutes, to allow the samples to equilibrate thermally, injection of part of the contents of each vial was carried out automatically. A flow rate of 1.0 ml/min and temperature of 140°C were maintained during the analysis.

The designation of samples that were characterised, their average molecular masses, polydispersities and melt flow indexes are summarised in Table 6.2.

Table 6.2: Characteristics of homopolymers and copolymers investigated

Materials	Comonomer content (%)	C2 or C5	M_w g/mol	M_n g/mol	Mw/Mn	MFI g/min
PP-1	-	-	373153	74631	5.0	16.5
PP-2	-	-	440668	85277	5.2	7.4
PP-3	-	-	489610	88247	5.5	4.7
PP-4	-	-	567710	95736	5.4	4.0
PP-5	-	-	588112	113099	5.2	3.8
PP-6	-	-	632176	126435	5.0	2.0
COP-1	1	C5	446923	85023	5.3	7.0
COP-2	2	C5	415298	83278	5.1	7.0
COP-3	3	C5	415608	76973	5.4	7.5
COP-4	4	C5	406325	78432	5.3	8.0
COP-5	3.9	C5	268557	50210	5.3	40.0
COP-6	3.9	C5	361761	67220	5.4	22.0
COP-7	3.9	C5	596295	97703	6.1	4.0
COP-8	3.9	C5	851702	137001	6.3	2.4
COP-9	3.1	C5	562270	116571	4.8	4.5
COP-10	2.5	C2	400553	60293	6,6	22
COP-11	3.5	C2	547720	91139	5.0	5.9
COP-12	5	C2	527451	86153	6.1	7.5
COP-13	1.5	C5	953005	221629	4.3	1.5
COP-14	1.5	C5	688173	163851	4.2	7.5
COP-15	1.5	C5	450610	102411	4.4	12.5
COP-16	3.5	C5	881006	209763	4.2	1.5
COP-17	3.5	C5	452661	105270	4.3	4.5
COP-18	3.5	C5	378273	92262	4.1	12.5
COP-19	5.5	C5	879628	209463	4.2	1.5
COP-20	4.9	C5	405880	76581	5.3	8.0
COP-21	3.5	C5	665082	110997	6.6	6.0
COP-22	4.9	C5	713416	107551	6.6	5.3
COP-23	5.9	C5	713555	86277	8.3	7.4
COP-24	3.5	C2	400553	60295	6.6	22
COP-25	0.63	C5	481651	81635	5.9	6.7
COP-26	0.96	C5	528787	98717	5.4	6.7
COP-27	2.0	C5	647296	125423	5.1	5.7

6.3 ANALYTICAL METHODS AND EQUIPMENT

Tabulated below the analytical methods and equipment used to determine the rheological, crystallisation, thermal, mechanical and physical properties of the polymer samples. The results of this study, comparing the properties of propylene/pentene-1 random copolymers with propylene/ethylene random and propylene homopolymers, are discussed in Chapters 7,8 and 9.

Table 6.3: Analytical methods and equipment used to determine polymer properties

Characteristic measured	Analytical method / equipment used	Comments
The melt flow index	ASTM D 1238 using a standard Melt Indexer.	
The molecular masses and distributions of molecular masses	Waters 150 CV GPC equipment with a data module and computer acquisition system.	
The molecular compositions of the copolymers	Perkin Elmer Patagon 2000 FTIR equipment.	
The rheological measurements	Controlled-stress Rheometric SR 500 dynamic rheometer with data module and computer acquisition system	Measuring head was a parallel plate system with diameter 2.5cm and 4 cm and a 1- mm gap size.
The steady-state viscosity curves, the creep curves and the components of complex modulus and complex viscosity	Orchestrator 6.4.4. (Rheometrics Sci.) software used to analyse the measured data.	Determined in temp. region: 190-230^{0}C. Samples produced in the form of injection moulded disks.
The glass transition temperature	Rheometric RSA II DMA equipment, in five frequencies.	Results were extrapolated to zero frequency.
(WAXD) experiments	Conducted with a Freiberger Prezisionsmechanik RTF equipment attached to a conventional X-ray source, which was equipped with a temperature-controlled sample holder.	Samples (0,3 mm thick, prepared by compression at 170 to 180°C) were tempered at 200 ^{0}C for 5 minutes, then cooled to the temp. of isothermal crystallization at a cooling rate of 20 ^{0}C/min. After crystallization, the samples were cooled to 25 ^{0}C.

The melting point, crystallization temperature and heat of fusion	Perkin Elmer DSC-7 equipment, in a nitrogen atmosphere	Before the isothermal crystallization process the samples (6±2 mg), in aluminium holders, were kept at 200 ^{0}C for 5 minutes to remove the residual thermal and crystallization history of the material, then cooled down to the isothermal crystallization temperature at a rate of 80 ^{0}C/min. The measuring time was five times the half crystallization time at the given crystallization temperature. After the crystallization process the samples were melted at a rate of 20 ^{0}C/min. The thermodynamic melting point was determined by the Hoffman-Week's method [8]. In this series of experiments the crystallization process was carried out to a low degree of crystallinity (about 15-20% relative crystallinity). A relatively high heating rate was used to avoid the effect of lamellae thickening and effect of post- and trans-crystallization. The peaks of the melting curves were taken as the melting points.
Tensile properties	Determined according to ASTM D 638 M.	
Izod (notched) impact strength was	Determined according to ASTM 256	
Density	Sartorius Specific Gravity Determination kit YDK 01	A sample is submerged in distilled water in the submersion beaker for 24 hours. It is then removed from the water, dried and weighed in air (Wa) after which the balance is zeroed, the sample submerged again and weight noted (Ww). Density (ρ) is determined using formula: $\rho = (Wa.\rho_w) / (0.99983.Ww) + 0.0012$ g/cm^3 where ρ_w is density of distilled water at measurement temp.

6.4 RESULTS AND DISCUSSION OF KINETIC STUDY

Shown below are the set of kinetic curves recorded during the propylene / 1-pentene copolymerisation reactions using the comonomer feed ratios as presented in Table 6.1.

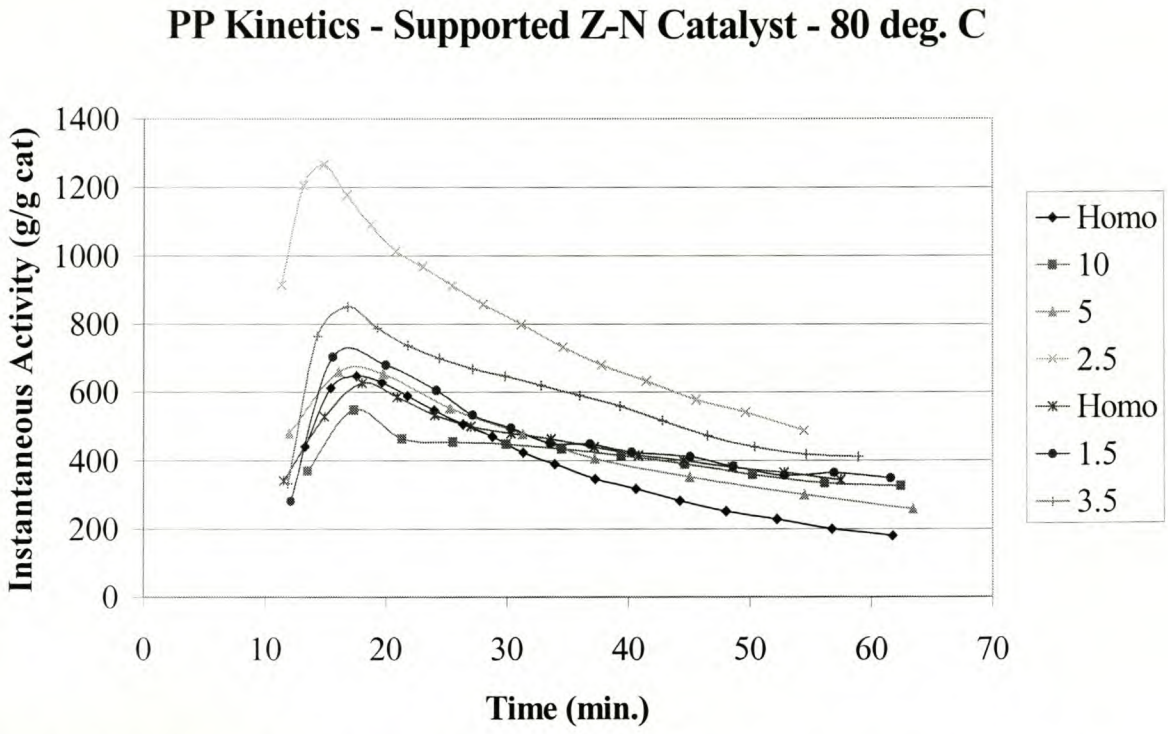

Figure 6.1: Instantaneous catalyst activity vs. reaction time for a range of fixed comonomer ratios

It was found that the activity of the $MgCl_2$ supported Ziegler-Natta catalyst generally increases with the introduction of 1-pentene as comonomer to the propylene polymerisation reaction. The increase in catalyst activity is observed for 1-pentene to propylene feed ratios of up to 5%. This is in line with the reported increase in catalyst activity when propylene is copolymerised with moderate amounts of ethylene, 1-hexene and other higher α-olefins [9, 10, 11]. The highest overall catalyst activity was achieved with a 1-pentene to propylene feed ratio of 2.5%. It can therefore safely be concluded that the maximum catalyst activity should be obtained with a feed ratio of between 1.5 and 3.5%

The integrated area under each curve is directly related to the productivity of the catalyst for a specific residence time in the reactor with the catalyst productivity being defined as amount of polymer produced by the amount of catalyst used, expressed in gram per gram. It is therefore of interest to note that the observed increase in catalyst activity is maintained over the entire polymerisation period of 60 minutes. As this time period is typical of the average residence time of catalyst in commercial reactors an increase of

catalyst productivity is expected during the manufacturing of random copolymers with an 1-pentene to propylene feed ratio of 5% or less.

It is of further interest to note that although the maximum catalyst activity achieved during the copolymerisation reaction with a feed ratio of 10% is slightly lower compared to that achieved for homopolymerisation, a higher average activity is maintained over the full duration of the reaction.

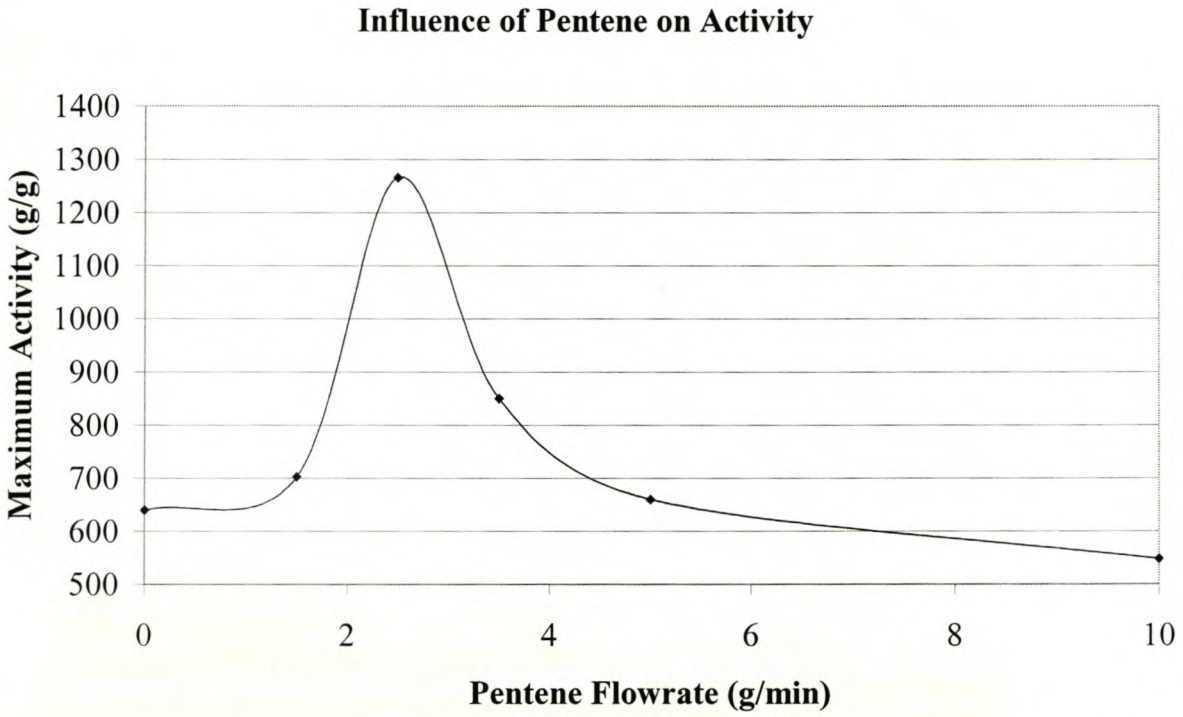

Figure 6.2: Relationship between maximum catalyst activity obtained vs. 1-pentene flow rate

The relationship between maximum catalyst activity achieved for different 1-pentene to propylene feed ratios during the copolymerisation of the two respected monomers is depicted in the Figure 6.2 above.

6.5 CONCLUSIONS

A lab-scale stirred bed gas-phase reactor system, designed for the preparation of olefin homopolymers and random copolymers using heterogeneous Ziegler-Natta catalyst systems, is described. A set of propylene homopolymers and random copolymers with ethylene and 1-pentene respectively as comonomer is synthesised under controlled conditions. The polymers are characterised with regard to their molecular weight and distribution as well as comonomer content to facilitate an in-depth study comparing their rheological, thermal, mechanical and physical properties.

During a study of the kinetic behaviour of propylene and 1-pentene copolymerisation reactions, using a $MgCl_2$ supported Ziegler-Natta catalyst system, an increase in the rate of polymerisation is observed. It is shown that the relationship of instantaneous catalyst activity over time is related to the overall productivity of a catalyst system. An 1-pentene to propylene feed ratio of 2.5% gave the highest instantaneous catalyst activity.

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CHAPTER 7

A COMPARATIVE STUDY OF THE RHEOLOGICAL THERMAL AND CRYSTALLISATION PROPERTIES OF PROPYLENE / 1-PENTENE RANDOM COPOLYMERS

7.1 INTRODUCTION

Polypropylene and its copolymers are used in a variety of processes to produce a wide range of products such as fibre, film, medical and food packaging. The proper selection of polymer microstructure is known to be crucial to each specific process application such as fibre spinning, injection moulding and extrusion. Today it can be stated without qualification that a good understanding of the rheological behaviour of polymer melts is an important prerequisite to optimise manufacturing and processing of resins [1].

This is due to the fact that thermoplastic materials are without exception processed via the molten state. Virtually all plastic manufacturing processes involve the application of a force or pressure to the polymer melt causing flow of deformation – in particular most processes involve applying a shear stress producing a movement measurable as a shear rate [2].

The flow behaviour of thermoplastic melts can be described as visco-elastic - characterised by both an elastic and viscous flow component [3]. However, their flow behaviour is essentially determined by the viscous component. Flow and viscosity curves are introduced to describe the relationship between the rheological behaviour of polymer melts and temperature, pressure and shear rate respectively. Flow curves depict the relationship between shear stress and shear rate. Viscosity curves describe the viscous behaviour of melts with viscosity being defined as the ratio of shear stress to shear rate with shear rate [1].

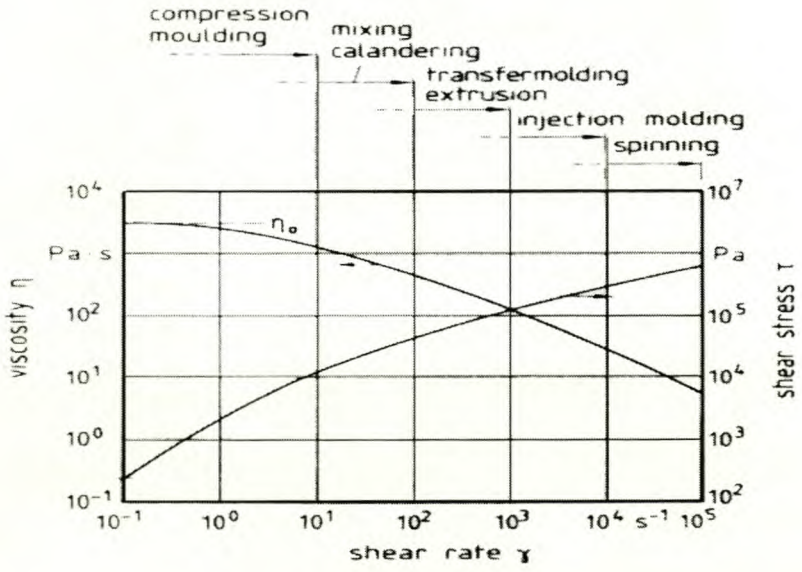

Figure 7.1: Flow and viscosity curves

Figure 7.1 above shows the flow and viscosity curves and shear rate range of some commercial conversion processes. The usual method of assessing processability, namely the Melt Flow Ratio (MFR) test, is conducted at very low shear rates which does not relate to processing shear rates. The influence of molecular weight (MW) and molecular weight distribution is well understood and described in literature [4, 5]. To study the effect of comonomer type and content on the rheological properties of PP random copolymers a control set of polymers, with tailored MW's and MWD's, was synthesised and characterised. These materials, used to compare the rheological properties of propylene / 1-pentene random copolymers to that of PP homopolymers and propylene / ethylene random copolymers, are listed in Table 6.1.

7.2 STEADY STATE AND DYNAMIC FLOW CURVES

Figures 7.2 and 7.3. show the viscosity and storage modulus curves for PP homopolymer and different 1-pentene- and ethylene-content random copolymers at a temperature of 200 ^{0}C. It can be seen from Figure 7.2 that the viscosities of 1-pentene copolymers are lower than the viscosities of the homopolymer but are higher than the viscosities of the ethylene copolymer. The viscosity of the pentene copolymers shows a higher shear and temperature sensitivity than the viscosity of the homopolymer and the shear sensitivity increases with an increase of pentene content. The shear viscosity and storage modulus are at a minimum at about 2% 1-pentene content. The homopolymer has the greatest viscosity and storage modulus while the ethylene copolymer has the lowest value in all the frequency regions investigated.

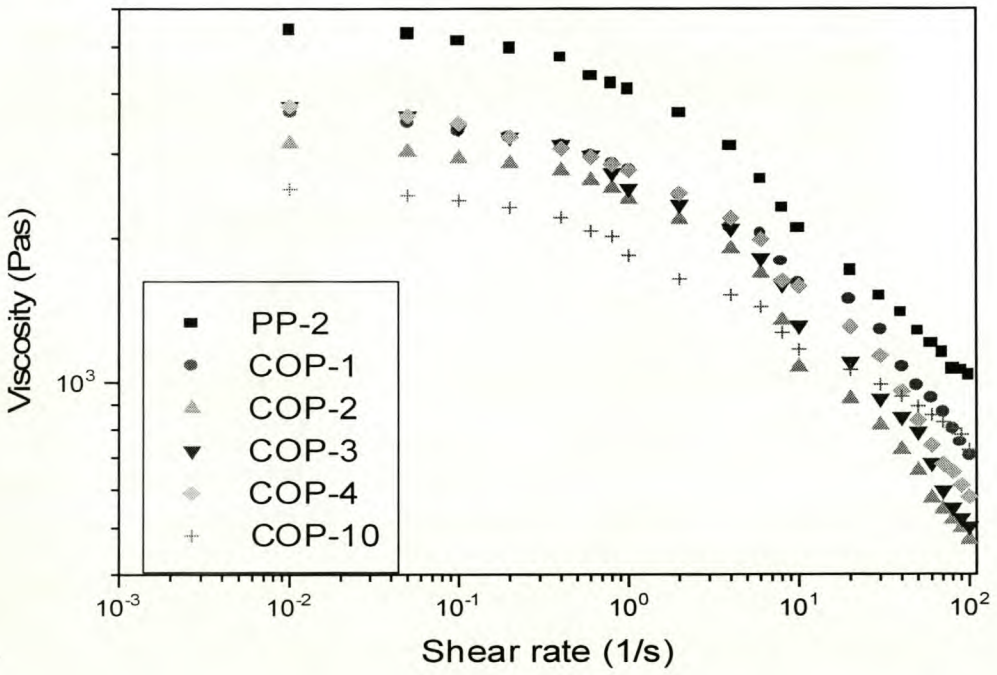

Figure 7.2: Flow curves for homopolymer and random copolymers with 1-pentene and ethylene as comonomer respectively at 200 ^{0}C.

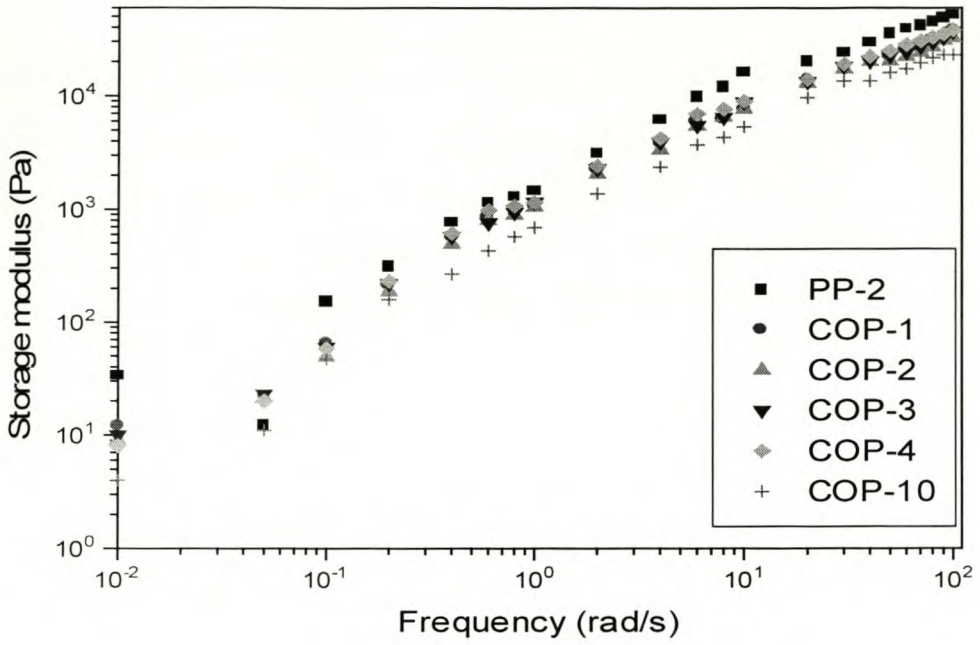

Figure 7.3: Storage modulus versus frequency for PP homopolymer, 1-pentene copolymers and ethylene copolymer at 190 ^{0}C.

The zero shear viscosity values were determined from the steady-state flow curves with the Carreau-equation [6, 7] by a standard least-mean-square-error method. A second method was to determine the zero shear viscosity from the dynamic measurements by the equation:

$$\eta_0 = \lim_{\omega \to 0} \frac{G''(\varpi)}{\omega} \qquad 7\text{-}1$$

A third possibility was to calculate the zero shear viscosity from the creep experiment via the slope of the steady-state part of the deformation curve (low stress region). Figure 7.4 depicts the zero shear viscosity versus the 1-pentene content for three series of samples. The zero shear viscosity values decrease with an increase in 1-pentene content, but in the 2-4% region a plateau is observed with not much change in the zero shear viscosities. The viscosity measurements for the respective homo- and random copolymers were conducted at 1, 10 and 100 s^{-1} shear rates. A minimum zero shear value for the propylene / 1- pentene random copolymers is noted at about 2% comonomer content.

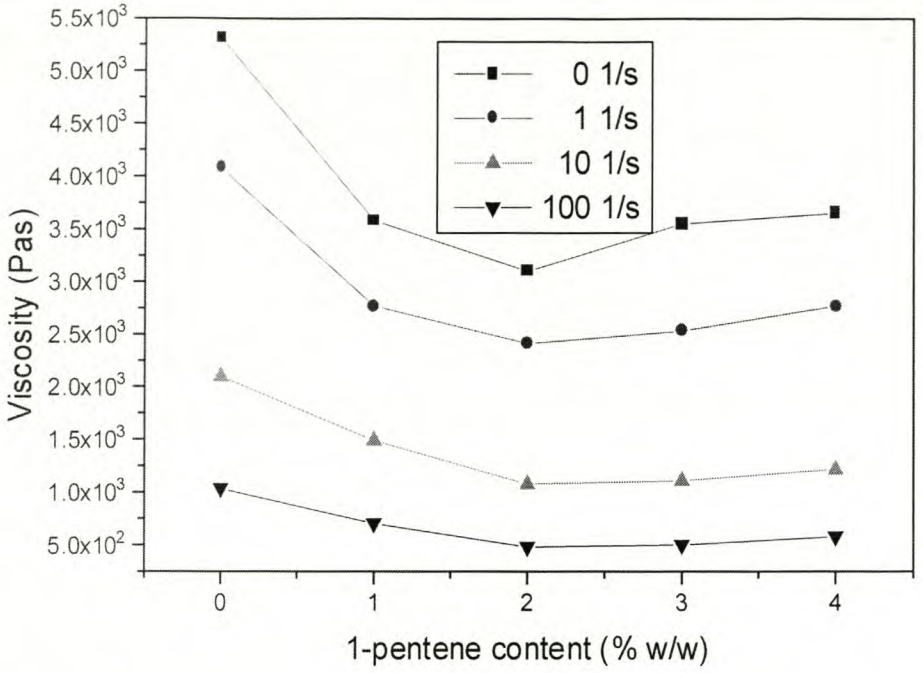

Figure 7.4: Zero shear viscosity, viscosities belong to 1, 10 and 100 s^{-1} shear rates at 200°C.

It is observed that in the temperature range studied, the temperature dependence of the zero shear viscosity can be described by an Arrhenius-type equation.

Activation energy or yield stress can be defined as the stress required initiating flow in a material. It can be measured by the extrapolation of the flow curve to the lower end of the shear rate scale – approaching zero shear rate. The activation energy of flow increased with the incorporation of 1-pentene into the polymer chain, and changed slowly with the amount of comonomer. The activation energy of homopolymer ranged between 38 and 44 kJ/mol, and that of the copolymers between 47 and 56 kJ/mol The results are listed in Table 7.1.

The zero shear viscosities were plotted versus the molecular mass, on logarithmic scale, for a series of homopolymers, five random copolymer samples with an 1-pentene comonomer content in the order of 3% and two random copolymers with 1.5 and 3.5% 1-pentene content respectively, all with different molecular masses. In each case a straight line was obtained, according to the well-known relationship:

$$\eta_0 = KM_w^a \quad if \quad M_w \geq M_c \qquad 7\text{-}2$$

The slopes of the respective straight lines (a) are 3.40 in the case of the homopolymer and 3.45 - 3.55 the case of the copolymers. The exponent increases slightly with an increase in 1-pentene content. The K values, summarised in Table 7.1, decrease with an increase in 1-pentene content.

The copolymers show a slightly greater molecular mass dependence than the homopolymers do.

Table 7.1: The values of K for homopolymers and copolymers with 1.5%, 3.5% and 3.9% 1-pentene content.

Materials	**Temperature ^{0}C**	**K_1.10 –16 (g/molPas)**
PP Homopolymers	190	5.71
	200	2.7 2
	210	2.70
	230	2.15
	190	2.25
1.5% 1-pentene	200	2.03
	210	0.85
	230	0.71
	190	0.93
3.5% 1-pentene	200	0.54
	210	0.27
	230	0.20
	190	0.65
3.9% 1-pentene	200	0.43
	210	0.28
	230	0.21

In some cases the molecular mass distributions were calculated from dynamic data by the Rheometrics Orchestrator 6.4.4. software. The software has the following relationship between the relaxation modulus and molecular mass distribution [8]

$$G(t) = G_N^0 \left[\int_0^\infty F^{1/2}(M,t) w(m) dM \right]^2 \qquad 7\text{-}3$$

where $F^{1/2}$ is the monodisperse relaxation function, *w(m)* a molecular mass distribution function, and G_N^0 is the plateau modulus. For the monodisperse relaxation function the software uses a single exponential form:

$$F^{1/2}(M,t) = \exp \frac{-t}{2\lambda(M)} \quad and \quad \lambda(M) = K_\lambda(T) M^b \qquad 7\text{-}4$$

where λ is the characteristic relaxation time which depends on the temperature and molecular mass. The temperature dependence can be described by an Arrhenius type equation, and the power exponent b is close

to the power exponent of average molecular mass dependence. The input parameters are the frequency dependent G' and G" values, the $K\lambda$ prefactor, a *b* power exponent and the plateau modulus. We started from the power exponent of equation (1) and used $K_\lambda = 2{,}8K / G_N^0$, where *K* is the proportionality constant in equation (2) summarised in Table 7.1 [9].

Figure 7.5 shows the molecular mass distributions calculated from the dynamic data compared with data obtained from the GPC method (for sample COP 2). Agreement in the lower molecular mass regions is not too good, but the calculated values describe the higher molecular mass region well.

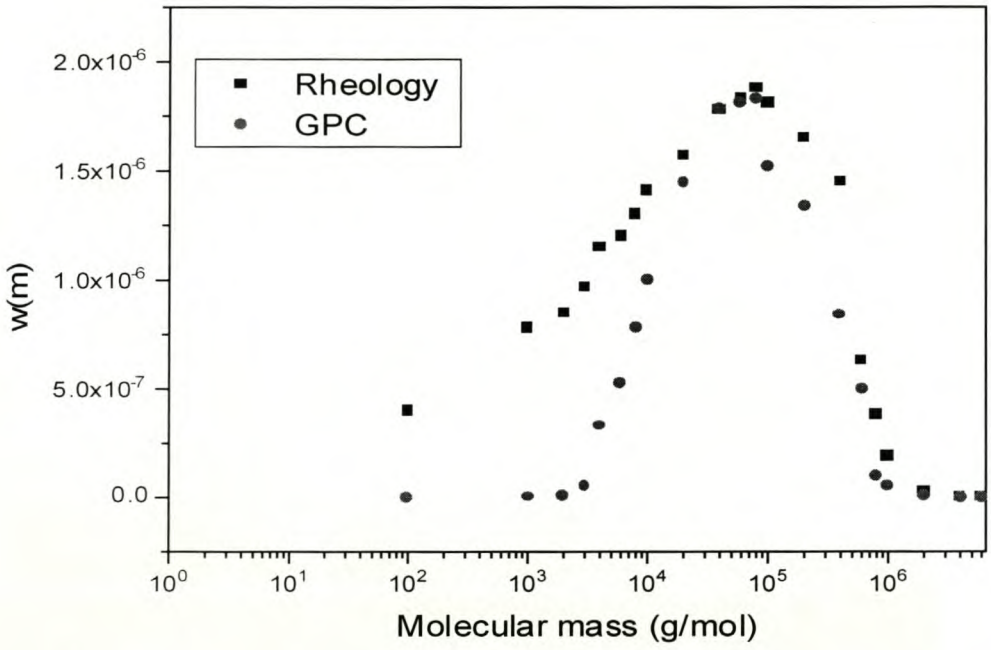

Fig 7.5: Molecular mass distributions calculated from GPC and rheological data of COP-2.

The MWD can theoretically be calculated from respectively the storage and loss modulus versus frequency relationship [10]. Figure 7.6 depicts the storage and loss modulus values versus frequency for a propylene / 1-pentene random copolymer, with 4% 1-pentene comonomer content, determined at 190°C. The storage modulus of the melt shows a stronger dependance with frequency than the loss modulus resulting in a point where the two moduli are equal. This point is referred to as the crossover point and the modulus and frequency as the crossover modulus and frequency respectively.

The polydispersity index (PI), which can be correlated to the ratio of the weight (Mw) to number (Mn) average molecular weight, can be calculated from the crossover modulus as follows [10]:

$$PI = 10^5 / G_C$$

Where G_C = G' = G'' at the crossover frequency and with modulus in SI units. Some of the calculated values are shown in Table 7.2 below.

Table 7.2: Measured crossover frequencies and moduli and calculated polydispersitiy values

Materials	Temperature	ω_c	G_C	PI
		Rad/s	KPa	
PP-1	210	20,9	18	5,2
COP-1	210	28,8	19	5,2
COP-2	210	30,1	20	5,0
COP-3	210	20,3	19	5,2
COP-4	210	17,8	19	5,2

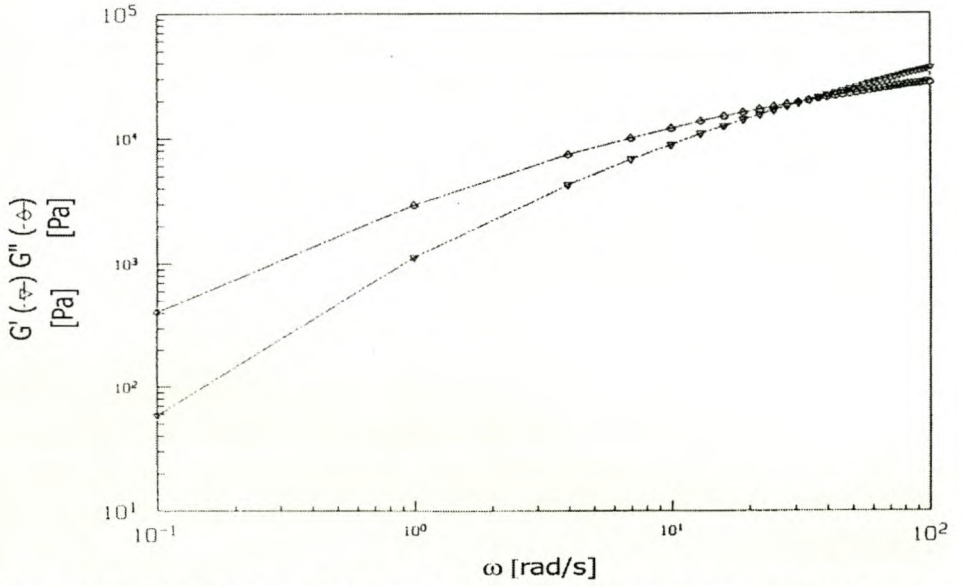

Figure 7.6: Typical storage and loss modulus curves versus frequency for a propylene / 1-pentene random copolymer

7.3 CREEP EXPERIMENTS

The steady state shear compliance was calculated from the creep measurements with the Orchestrator 6.4.4 software. The steady state shear creep compliance could also be calculated from the dynamic measurements:

$$J_0 = \frac{1}{\eta_0^2} \lim_{\omega \to 0} \frac{G'(\omega)}{\omega^2} \qquad 7\text{-}5$$

The steady shear compliance showed an increase with the 1-pentene content and reached a maximum value at about 2% 1-pentene content, then decreased with an increase in 1-pentene content. The ethylene copolymer had a higher steady state creep compliance than the 1-pentene copolymers.

7.4 PLATEAU MODULUS

The plateau modulus is a very important parameter in the determination of a relationship between the chain dimension and viscoelastic properties [11-15]. From the plateau modulus can be determined the molecular mass, between the network junction points, by the equation:

$$M_e = \frac{4\rho RT}{5G_0} \qquad 7\text{-}6$$

The molecular mass between network junction points (or between entanglements) relates to the chain dimension (11):

$$M_e = B^2 \left[\frac{\langle R^2 \rangle_0}{M} \right]^{-3} \rho^{-2} N_A^{-2} \qquad 7\text{-}7$$

where *B* is a constant, $\langle R^2 \rangle_0$ is the unperturbed mean-square end-to-end distance, M is the molecular mass, ρ is the density and N_A is the Avogadro-number. Witten, Milner and Wang [16] have defined a quantity termed 'packing length' (p) which is used to denote the number of individual chains present in a given small volume of the melt. This parameter is given as:

$$p = \frac{M}{\langle R^2 \rangle_0 \rho N_A} \qquad 7\text{-}8$$

and hence is intrinsically related to the size of the polymer coil and the volume that it takes up.

From the equations (7-6), (7-7) and (7-8) we get:

$$G_N^0 = \frac{4B^2 kT}{5p^3} \qquad 7\text{-}9$$

Lin [17] has defined a constant, n_t, which is the number of entanglement strands in a cube with side d_t. This is given by:

$$n_t = \rho N_A \left[\frac{\langle R^2 \rangle_0}{M} \right]^{3/2} M_e^{1/2} \qquad 7\text{-}10$$

where the value of n_t is 21.3±7%.

From the equations (7-7) and (7-10) it follows that $B = 1/n_t$.

Fetters at al. (11) have found a general relationship that is independent of temperature and polymer species between the molecular mass between entanglement and packing length:

$$M_e = 218 \rho p^3 \qquad 7\text{-}11$$

A relationship beween the critical molecular mass and packing length was found [14]:

$$\frac{M_c}{M_e} = \left(\frac{p^*}{p} \right)^{0,65} \qquad 7\text{-}12$$

in which $p* = 9.2 \cdot 10^{-8}$ cm. From the packing length, the reptation tube diameter can also be calculated by the equation:

$$19p = d_t \qquad 7\text{-}13$$

The plateau modulus can be used to calculate the packing length, molecular mass between the entanglement, and tube diameter. The Plateau modulus can be obtained from the dynamic measurement via integration of G" versus frequency plot, or from the following empirical relation [15]:

$$G_N^0 = 3,56 G''_{\max} \qquad 7\text{-}14$$

The plateau modulus may be determined from the creep experiment via the steady- state shear creep compliance with equation [9]:

$$G_N^0 = \frac{1,7}{J_0} \qquad 7\text{-}15$$

In most cases evaluated, the maximum value of loss modulus had not been reached. In only some cases (for PP-2, PP-3, COP-13, COP-14 and COP-15) a maximum on the loss modulus curves and the plateau modulus was determined by the equation (14). On using equation (15) to determine the same plateau modulus values, the calculated values were smaller than the measured ones. It was suspected that the deviation arose from the effect of polydispersity. On the basis of the measured plateau modulus and the measured steady creep compliance the following equation for the steady-state shear creep compliance is proposed:

$$J_0(measured) = J_0 \left(\frac{M_w}{M_n} \right)^{2,2} \qquad 7\text{-}16$$

From the measured steady shear compliance the steady state homodisperse shear creep compliance was calculated, and from this value the plateau modulus was determined by equation (16). The plateau modulus values, the calculated <Ro>/M ratio, the packing length, molecular mass between

entanglement points versus 1-pentene content are summarised in Tables 7-3 and 7-4.

Table 7.3. The measured steady-state shear creep compliance (J_0) and plateau modulus, the calculated plateau modulus values and activation energy

Materials	Temp. ^0C	J_0 10^{-4} 1/Pa	G^0_N MPa calculated	G^0_N MPa Measured	E KJ/mol
	190	1.38	0.460	0.440	
PP-2	200	1.40	0.430	0.430	34,8
	210	1.50	0.420	0.420	
	230	1.50	0.420	0.440	
	190	1.85	0.396		
COP-1	200	1.70	0.384		47,8
	210	1.70	0.384		
	230	1.80	0.363		
	190	3.00	0.202		
COP-2	200	3.20	0.189		50,2
	210	3.40	0.178		
	230	3.40	0.178		
	190	2.50	0.283		
COP-3	200	2.80	0.253		54,5
	210	2.80	0.253		
	230	2.80	0.253		
	190	1.80	0.363		
COP-4	200	2.00	0.327		51,8
	210	2.00	0.327		
	230	2.20	0.297		
	190	4.00	0.265		
COP-10	200	4.20	0.253		59,5
	210	4.60	0.231		
	230	5.30	0.216		
	190	0.98	0.407	0.390	
COP-13	200	1.00	0.393	0.390	53,8
	210	1.07	0.393	0.385	
	230	1.10	0.380	0.390	
	190	1.10	0.363	0.375	
COP-14	200	1.20	0.341	0.380	42,9
	210	1.10	0.373	0.360	
	230	1.10	0.373	0.370	
	190	1.20	0.379	0.370	
COP-15	200	1.10	0.408	0.360	45,0
	210	1.20	0.365	0.380	
	230	1.30	0.357	0.390	

It can be seen that the 2% 1-pentene content random copolymer has the smallest plateau modulus.

Table 7.4. Molecular and rheological parameters calculated by molecular simulation software at 200°C

Materials	$\langle R^2 \rangle_0 / M$ 10^{-8} $cm^2 mol/g$	Density g/cm^3	p 10^{-8} cm	M_e g/mol	G_0 MPa	d_t 10^{-8} cm	M_c g/mol
Homopolymer	0.698	0.760	3.19	5377	0.444	62.19	10705
1% 1-pentene	0.695	0.758	3.21	5760	0.435	62.63	10853
2% 1-pentene	0.432	0.756	5.18	24113	0.104	101.01	33296
3%1-pentene	0.565	0.754	3.97	10836	0.230	77.44	17748
4% 1-pentene	0.612	0.753	3.67	8549	0.291	71.59	14766
5% 1-pentene	0.678	0.752	3.32	6304	0.395	64.70	11627

7.5 CONCLUSIONS

The propylene / 1-pentene random copolymers show interesting rheological behaviour. The rheological parameters showed an extreme value at around 2% comonomer content which can be correlated to the change in the size of the polymer coil. These random copolymers contain some bulkier branches than propylene / ethylene random copolymers. The effect of these bulkier group is two-fold:

- They increase the free volume between chains. Because the volume is closely related to visosity we would expect the chain with longer branches to have greater mobility, because there is more space for movement of the segments. On the other hand,
- The bulkier groups should generally require more stress to move

.

The experimental data showed that the increase in free volume plays an important role in the low pentene content region. Above 4% 1-pentene content the viscosity and elasticity increase for the random copolymers of similar molecular weight and distribution.

From a processing point of view the copolymers show a similar behaviour compared to homopolymers in general. However, below 2% 1-pentene content there is a reduction in the zero shear viscosity if compared to homopolymers of similar molecular weight and distribution. Copolymers with a pentene content above 4% on the other hand, show an increase in zero shear viscosity compared to homopolymers. The propylene / 1-pentene random copolymers generally have better processability than ethylene copolymers because of the higher shear and temperature sensitivity of their rheological parameters.

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CHAPTER 8

A STUDY OF THE THERMAL AND CRYSTALLISATION PROPERTIES OF PROPYLENE / 1-PENTENE RANDOM COPOLYMERS

8.1 INTRODUCTION

Polypropylene has a relatively high glass transition temperature that limits its application. Copolymerisation decreases the Tg by introducing irregularities to the polymer backbone. These irregularities not only affect the macroscopic properties such as toughness or transparency, but also the microscopic ones.

There are many references in the literature (1-5) concerning morphology and crystallinity investigations of propylene / alpha- olefin random copolymers. Generally propylene / ethylene and propylene / 1-butene random copolymers are the subjects of these studies because of their great industrial importance. The influence of randomly dispersed comonomer units on the crystal structure and properties can be summarised as follows:

- Together with the usual alpha polymorph, the unique gamma crystalline form appears [3, 6].
- Generally an increase in the comonomer content in propylene / alpha-olefin random copolymers results in a decrease in crystallinity (and increase in the ratio of the gamma to alpha phase).
- The increase of isothermal crystallisation temperature or decrease in cooling rate favours an increase in the ratio of the gamma phase.
- The comonomer content also results in a decrease in melting temperature, equilibrium melting temperature and melting enthalpy.

The thermal and crystallisation properties of propylene / 1-pentene random copolymers are characterised and a study of the morphology presented as a function of comonomer composition and crystallisation temperature and compared to the properties of other propylene / alpha-olefin random copolymers.

8.2 THERMAL PROPERTIES

A very well known fact is that the melting temperatures of random copolymers are lower than homopolymers [7]. The decrease in melting temperature is proportional to the amount of comonomer and degree of supercooling. The thermodynamic melting point of the copolymer can be calculated from the following equation 8-1 [8]:

$$\frac{1}{T_m} - \frac{1}{T_m^0} = \frac{R}{\Delta H_m}(1-x) \qquad (8\text{-}1)$$

where: T_m and T_m^0 are the thermodynamic melting points of random copolymer and homopolymer, respectively, ΔH_m is the heat of fusion of a 100% crystalline homopolymer, 8790 J/mol [9], x is the mole fraction of comonomer, and R is the gas constant. Using equation (8-1) a 2,0°C/mol% decrease in thermodynamic melting point was obtained, independent of the type of comonomer. Avella [10] and Laihonen [11, 12] have found values of 2,1 and 2,3°C per mole% comonomer for propylene / ethylene random copolymers, respectively, which are very close to the theoretical values. In the case of propylene / 1-butene random copolymers a value of 2,0°C per mole% comonomer was measured [13].

The determination of the thermodynamic melting points of propylene / 1-pentene random copolymers by the Hoffman Weeks method [14] is displayed in Figure 8.1. The results are summarised in Table 8.1.

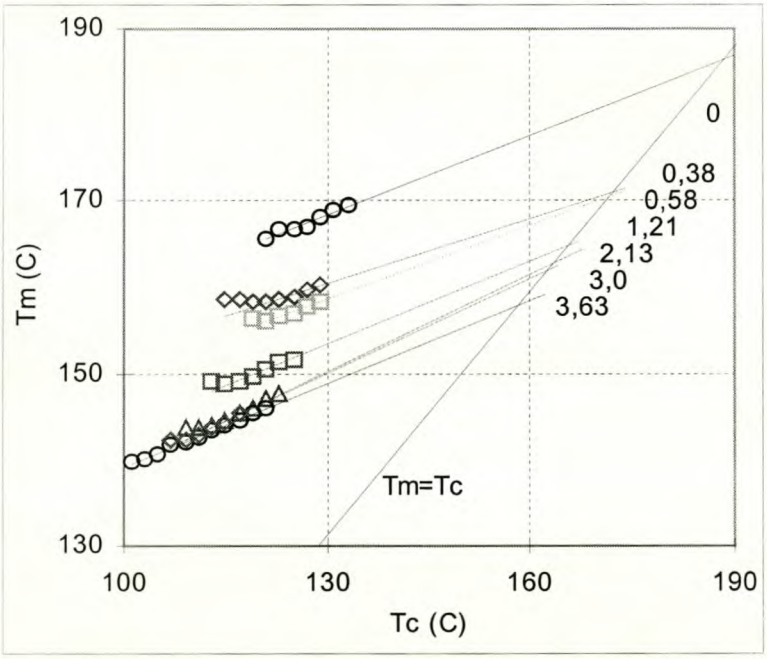

Figure 8.1. Determination of thermodynamic melting points of propylene / 1-pentene random copolymers by Hofmann-Weeks-method. The numbers indicate the 1-pentene comonomer content in mol%.

Table 8.1. Thermodynamic melting points, heats of fusion and glass transition temperatures dependent on the 1-pentene content in random copolymers

1-pentene content (mol %)	T_m^0 (^{0}C)	ΔH_m^0 (J/g)	T_g (^{0}C)
0.00	185.5	146	9.5
0.38	170.7	157	9.0
0.58	169.9	148	8.7
1.21	164.5	138	8.0
2.13	162.6	121	7.5
3.00	161.7	115	7.0
3.63	157.9	105	6.5

The depression in the equilibrium melting point (T_m^0) of propylene / 1-pentene random copolymers with comonomer content, compared to ethylene and 1-butene random copolymers, is illustrated in Figure 8.2. The depression in the T_m^0 of the propylene / 1-pentene random copolymers with increasing comonomer content is much more pronounced compared to the other copolymers under discussion. It is also non-linear and deviates from the theoretical trend as calculated by equation 8.1.

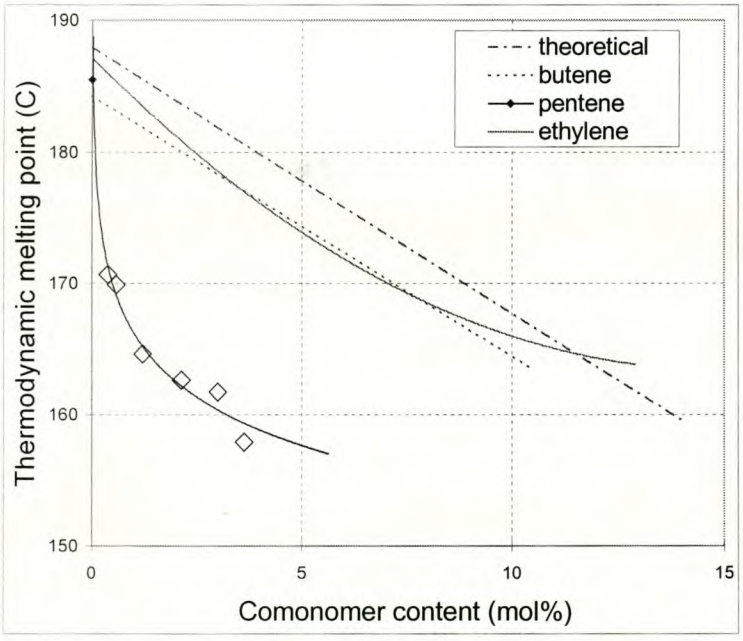

Figure 8.2: The relationship between thermodynamic melting points of propylene-α-olefin copolymers and the comonomer content

The melting enthalpy, according to literature and own results, decreases with increasing comonomer content [15]. The thermodynamic heat of fusion, however, does not exhibit such an unambiguous tendency. In the case of

propylene / ethylene random copolymers Avella [10] observed a 9 J/g decrease in the normalised heat of fusion per mole% increase in comonomer content in the 0 - 11,9 mole% comonomer range. Laihonen [11] obtained a smaller value of 4 J/g per ethylene mol% increase. In the case of propylene / 1-pentene random copolymers a value of 13 J/g per 1-pentene mol% increase was observed.

The glass transition temperatures were almost constant, and showed very little decrease with an increase in 1-pentene content - as can be seen from Table 8.1. A decrease in glass transition temperature was more significant in the case of the propylene / ethylene random copolymers.

8.3 CRYSTALLINITY AND CRYSTAL MODIFICATIONS

A homopolymer and 6 propylene/pentene random copolymers with different pentene contents (0.38 – 3.63%) were investigated. The polymers investigated are listed in Table 8.2 below.

Table 8.2: Comonomer content, number-average molecular mass and melt flow index (MFI) of propylene / 1-pentene random copolymers analysed for crystallisation and morphology

C5 %	C5 mol%	Mn (g/mol)	MFI
0 (PP-2)	0	440 668	7,4
0.63	0,38	481 651	6,7
0.96	0,58	528 787	6,7
2.0	1,21	647 296	5,7
3.5	2,13	665 082	6,0
4.9	2.94	713 416	5,3
5.9	3,63	713 555	7,4

The degree of crystallisation was determined by the WAXD method as described in Chapter 6. The α, β, and γ modifications, as described in section 5.4.2.3 have peaks on the measured spectrum at diffraction angles (2θ) 14 – 19^0, 15-16,1^0 and 19,5-20,5^0 respectively. The ratio of amorphous to crystalline phases, based on Weidiger's method [16], is used to determine overall crystallinity. A method proposed by Mezghani [3] was used to calculate the relative content of the γ modification. In this method the $A_\gamma/(A_\gamma + A_\alpha)$ area ratio of the characteristic peaks of the α and γ modifications respectively (18-19^0 for α, 19,5-20,5^0 for γ-form) is used to determine the relative γ content. Although the values obtained by this method aren't exact, because of the slight overlay of neighbouring peaks, the error is constant and as such shows good correlation.

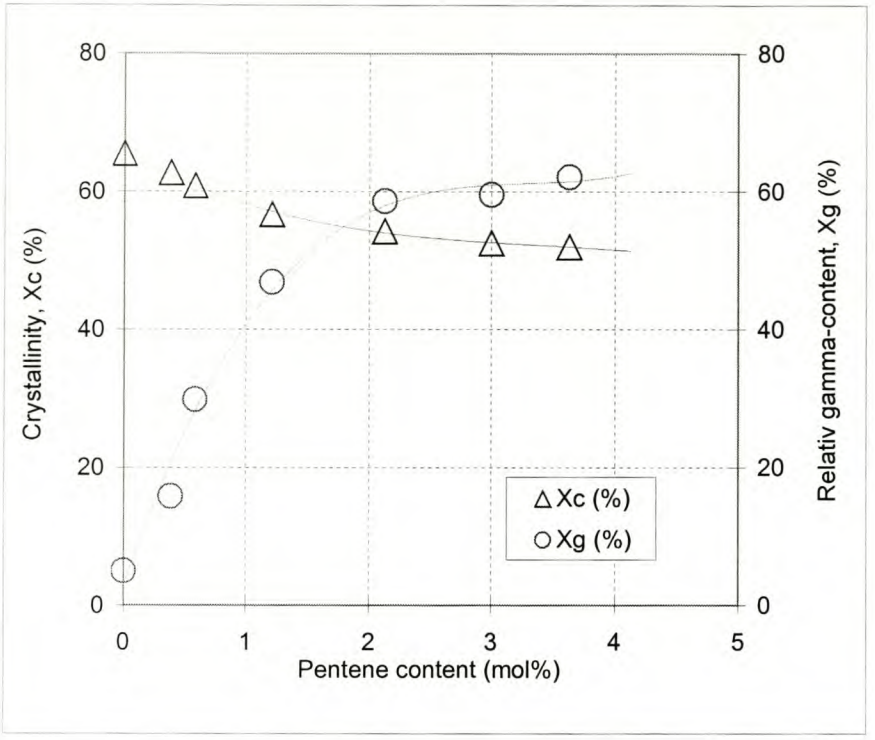

Figure 8.3: Degree of crystallinity and relative gamma content versus 1-pentene content.

Figure 8.3 displays the degree of crystallinity and the relative gamma content of the samples as a function of the 1-pentene content. Each sample was crystallised at the temperature that belongs to the ten-minute half time of crystallisation. It can be observed that after a sharp initial decrease, the crystallinity shows a 1,5% decrease per mole% increase in 1-pentene content, which is very similar to the 1% decrease per mole% increase in the ethylene comonomer content [2, 12].

From the moderate decrease in crystallinity and from the small expansion of the crystal unit cell Turner-Jones [1] and Laihonen [12] drew the conclusion that low levels of randomly distributed ethylene units are able to co-crystallise with the polymer units. The same tendency was observed in the case of 1-butene comonomer [13], while 1-hexene decreases the crystallinity with 18% per mol % [5]. This shows that the increase in the size of the comonomer beyond a certain limit hinders the co-crystallisation and this leads to a considerable decrease in the crystallinity.

The results indicate that the propyl side group of the 1-pentene comonomer is the largest group that can be included in the crystals. The butyl group side group of propylene / 1-hexene random copolymers exceeds this limit and causes the disruption of crystallinity.

The gamma content of the samples showed the expected increase with the comonomer content, which confirms that the structural heterogeneities help

the formation of the gamma crystal form. The ratio of the γ form increases with pentene content three times faster than in propylene/ethylene copolymers. This supports the assumption that the size of the side group has a great impact on the formation of the γ modification.

Isothermal crystallisation was performed on the 3.63 mol% sample at a range of crystallisation temperatures (function of supercooling). The results are presented in Figure 8.4. The degree of crystallinity remained unchanged in the studied temperature range, but the γ content increased from the initial 48% to 65% with an increase in crystallisation temperature. The increase in the γ content (with practically constant total crystallinity) shows that the formation of the γ form is favoured at higher crystallisation temperatures.

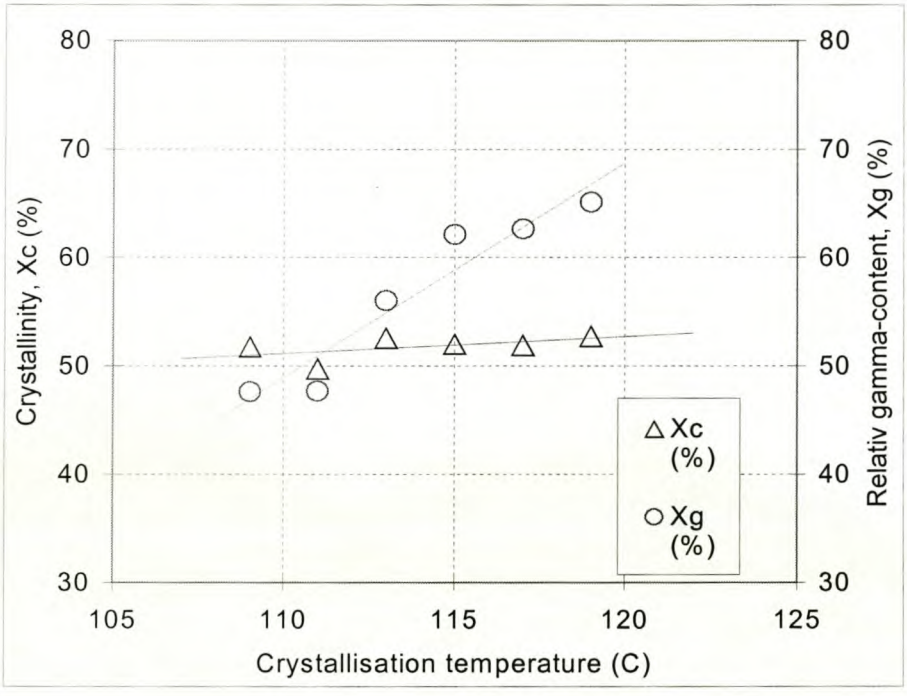

Figure 8.4: Crystallinity and relative gamma content of a propylene / 1-pentene random copolymer (3.63 mole% comonomer content) as a function of isothermal crystallisation temperature

It should be noticed, however, that most of the studied samples contain both α and γ modification, which have different heats of melting. To prove this the thermodynamic heat of fusion was plotted against the γ content for a propylene / 1-pentene random copolymer (3.63 mol% comonomer content) crystallised at different temperatures. From Figure 8.5 it is evident that a linear correlation exists.

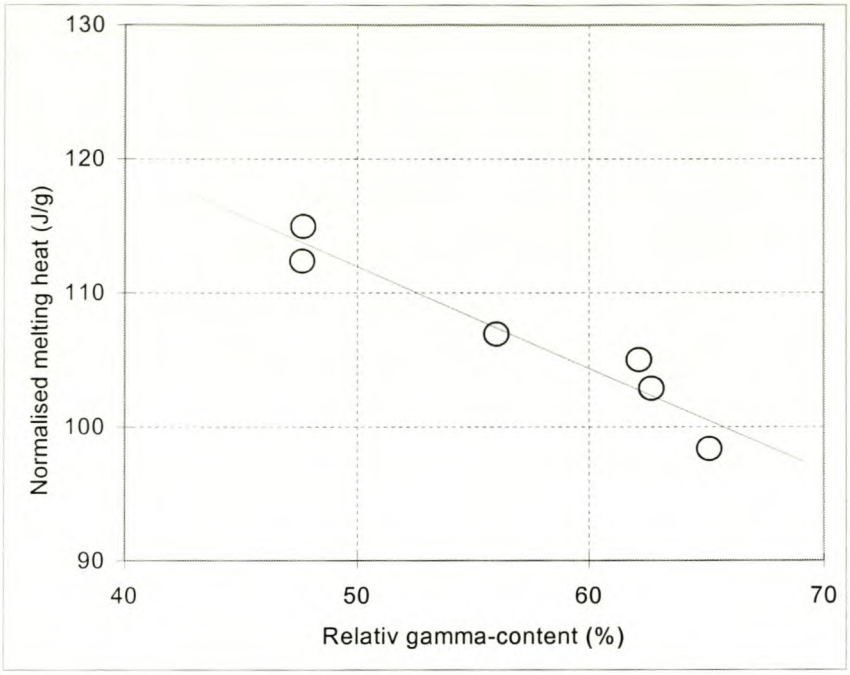

Figure 8.5 The normalised heat of fusion of propylene / 1-pentene random copolymer with 3.63 mole% 1-pentene content versus relative gamma content

The DSC thermograms of the isothermally crystallised samples are shown in Figures 8.6 and 8.7. In contrast to the homopolymer, all the random copolymers exhibit bimodal melting. The ratio of the peak areas is approximately the same as the relative γ content measured by WAXD (compare with Figures 8.3 and 8.4). Results published by Kardos [17] and Pae [18], on the melting point of the γ crystalline form, indicate that the lower melting peak can be attributed to the heat of fusion of the γ phase.

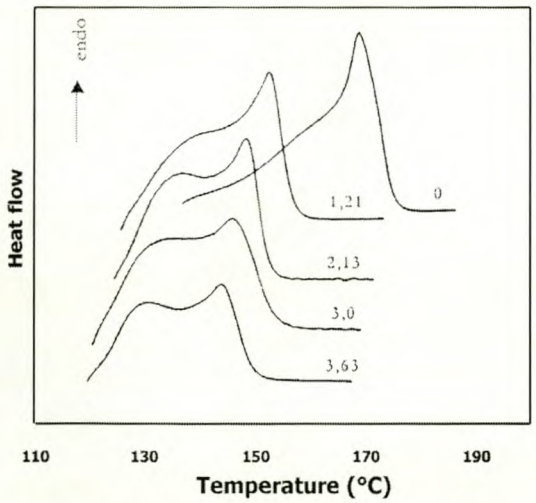

Figure 8.6: Melting thermograms of 1-pentene random copolymers

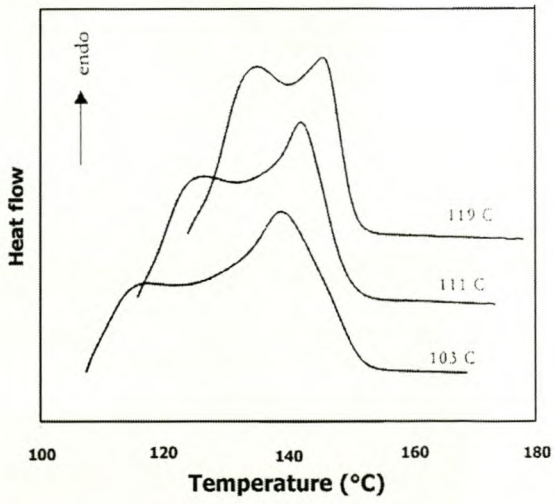

Figure 8.7: Cryst. thermograms of 1-pentene random copolymers

8.4 CONCLUSION

Introduction of 1-pentene as comonomer into isotactic polypropylene resulted in the formation of the γ crystal structure. The γ to α polymorph ratio observed was much higher than reported ratios for polypropylene random copolymers with ethylene or butene as comonomers respectively. According to our measurements, 1-pentene is the highest α-olefin that can be included in the crystal phase. The equilibrium melting point decreases with pentene content in a non-linear fashion and the values are much lower than the theoretical ones. It is shown that the thermodynamic heat of fusion depends on not only the type of crystal modification but also on the comonomer type and content.

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CHAPTER 9

THE MECHANICAL AND PHYSICAL PROPERTIES OF PROPYLENE / 1-PENTENE RANDOM COPOLYMERS

9.1 INTRODUCTION

The physical properties of all polyolefins, including PP, such as modulus, tensile strength, elongation, hardness, impact strength, density, transparency, melting temperature etc. primarily are a function of molecular weight and distribution as well as crystallinity [1]. This relationship between molecular structure and the physical properties of crystalline PP is a well researched topic with several research groups reporting on the profound influence that these variables have on the properties of crystalline polymers [1, 2, 3, 4].

PP homopolymer is a relatively rigid material with a high melting point and poor transparency and impact strength. To modify the properties and broaden the application field of this resin, controlled branching is introduced into the polymer backbone. This is achieved with the copolymerisation of propylene with usually ethylene and/or 1-butene to produce materials with improved transparency, higher flexibility and lower melting points [5, 6]. Although most commercial PP random copolymers employ ethylene and to a much lesser degree 1-butene as comonomer, the use of 1-hexene as comonomer has also been investigated [6].

In previous presentations, based on preliminary findings, the opportunities of using 1-pentene as comonomer in the PP random copolymer market was presented [7, 8]. In this study the physical properties of propylene / 1-pentene random copolymers as a function of the degree of branching are investigated and compared to propylene / ethylene random copolymers.

A set of PP homopolymers and propylene random copolymers with ethylene and 1-pentene as comonomers respectively, was synthesised and characterised with regard to comonomer content, molecular weight and distribution as well as melt flow ratio (MFR). These materials and the analytical methods used to determine their physical properties, unless otherwise specified, are described in Chapter 6.

9.2 MECHANICAL PROPERTIES

9.2.1 Tensile Modulus

The influence of the crystallinity of propylene polymers on modulus was described by Menges et. al. [9]. It was shown that there is a direct relationship between modulus and crystallinity. The relationship between comonomer type and content and crystallinity was studied and the results reported and discussed in Chapter 8. Our experimental data confirm the decrease in tensile modulus with an increase in 1-pentene content and therefore decreased crystallinity as shown in Figure 9-1 below.

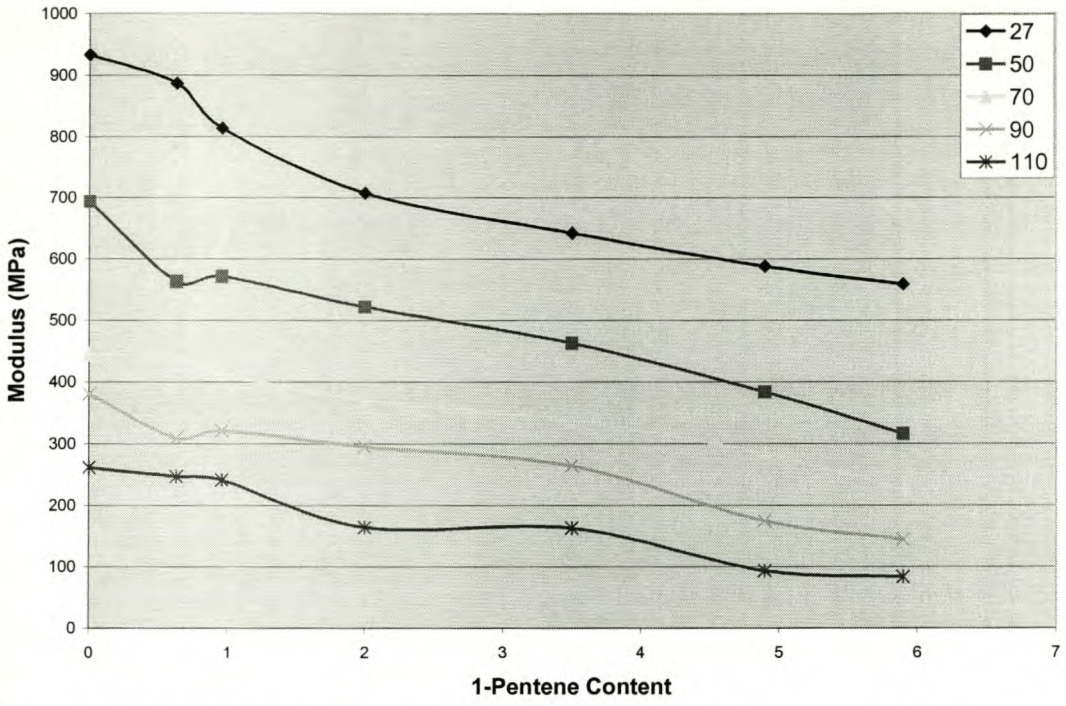

Figure 9.1: Tensile modulus of propylene / 1-pentene random copolymers as a function of comonomer (1-pentene) content

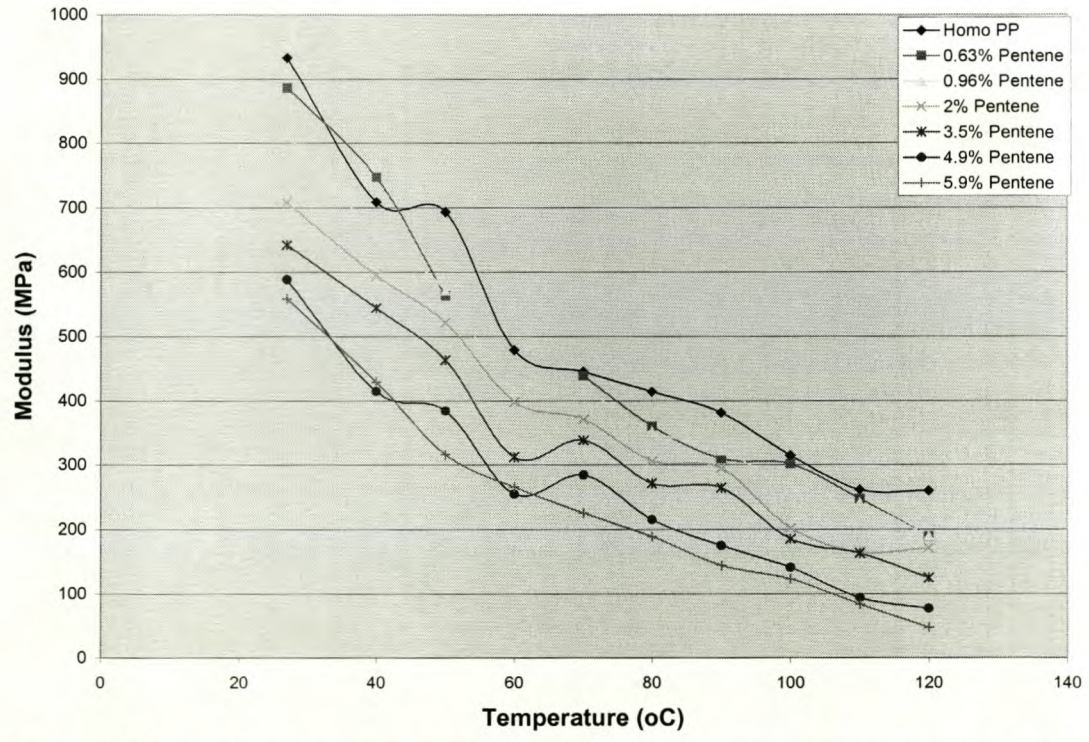

Figure 9.2: Tensile Modulus as a function of temperature for a range of propylene / 1-pentene random copolymers

The moduli of propylene random copolymers with ethylene and 1-pentene as comonomers respectively, were compared and the results presented as Figure 9.3. Random copolymers with similar MFR's and comonomer content, on a weight% basis, were selected for evaluation.

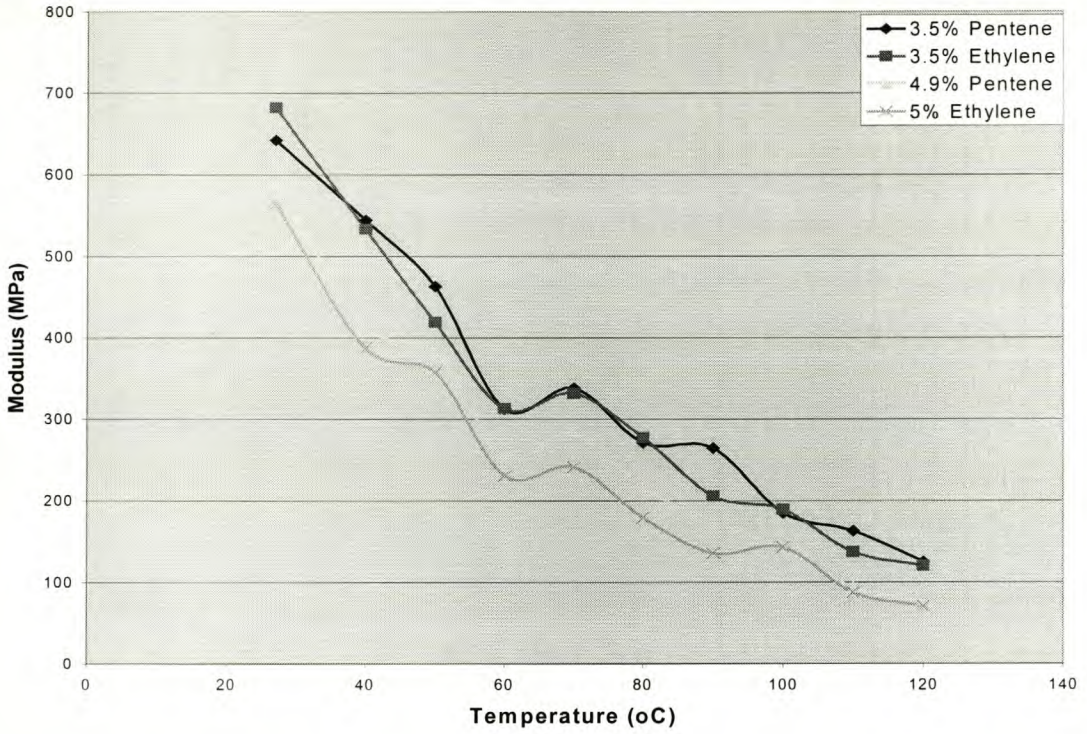

Figure 9-3. Tensile modulus at different temperatures versus comonomer content.

The stiffness of propylene random copolymers with 1-pentene and ethylene as comonomers and equal comonomer content (weight%) are remarkedly similar over a wide temperature range. These results strongly support the conclusion the propyl branches of the propylene / 1-pentene random copolymer are able to co-crystallise with the propylene polymer units and are not excluded from the crystal structure. Wiberg et. al. reported that the butyl side branches of propylene / 1-hexene random copolymers are excluded from the crystal structure resulting in a dramatic drop in crystallinity and consequently stiffness [10]. As a relationship was identified between the length of the side branch and transparency, at similar comonomer content levels on a weight% basis (section 9.3), **propylene / 1-pentene random copolymers offer the unique combination of stiffness and clarity not obtainable with other comonomers.**

9.2.2 Tensile strength and elongation properties

In Figure 9.4 the yield strength of propylene / 1-pentene random copolymers is shown at different temperatures as a function of comonomer content. It is seen that the tensile strength at yield decreases with increase in comonomer

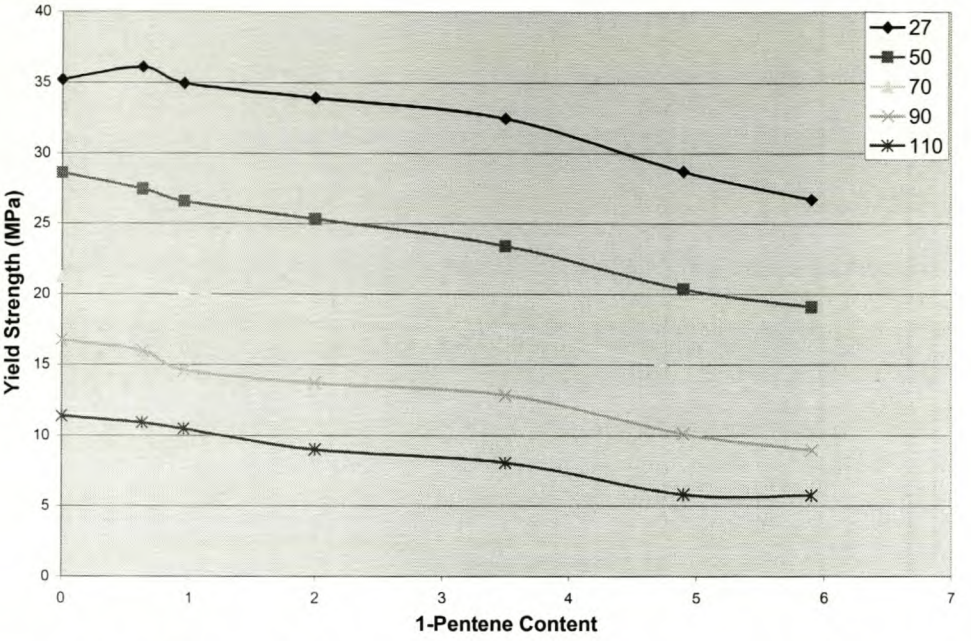

Figure 9.4: Yield strength of propylene / 1-pentene random copolymers as a function of comonomer content at a range of temperatures

content and the resultant decrease in the crystallinity. Figure 9.5 depicts a comparison of the yield strengths of propylene random copolymers with ethylene and 1-pentene as comonomer respectively. Propylene / 1-pentene random copolymers exhibit higher yield strengths than ethylene copolymers over the temperature range covered.

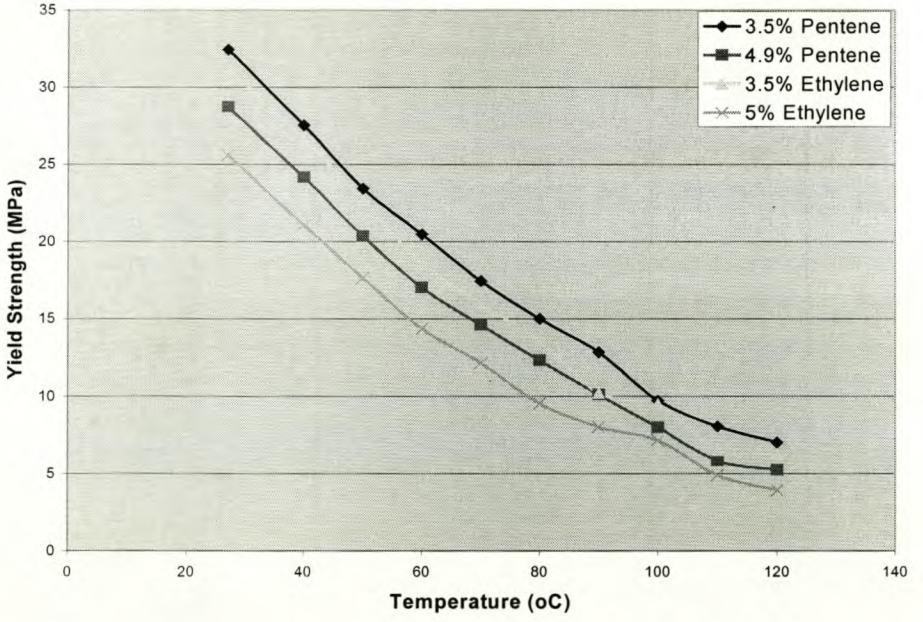

Figure 9.5: Comparison of tensile yield strengths of propylene random copolymers with ethylene and 1-pentene as comonomer respectively

Values for elongation at yield are mainly between 10 and 15% for low 1-pentene content, but values are high as 30% were obtained for copolymers containing high amounts of 1-pentene. In general, the elongation of random propylene/1-pentene copolymers is higher than that of random propylene/ethylene copolymers. The elongation at break for a range of random copolymers is shown below in Figure 9.6.

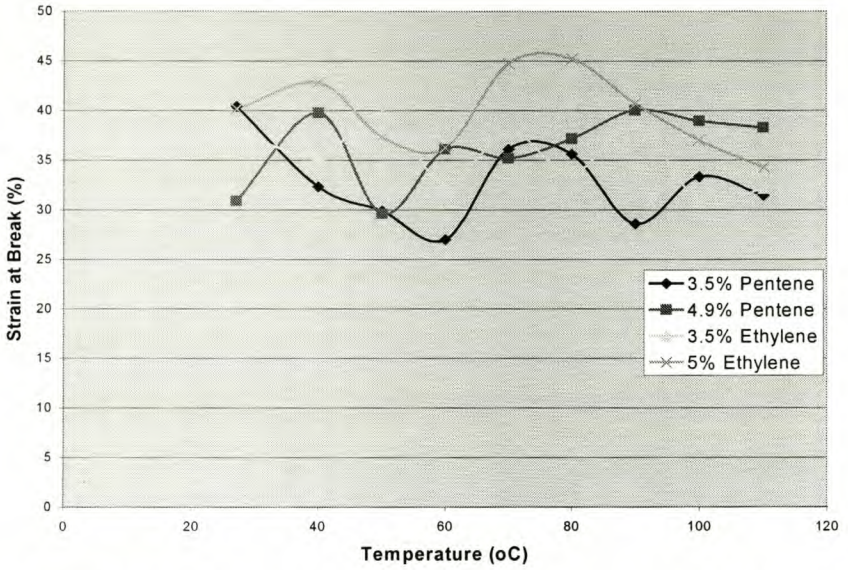

Figure 9.6: Strain at break for propylene random copolymers with ethylene and 1-pentene respectively as comonomers at comparative comonomer levels

9.2.3 Impact Strength

The strong relationship between the crystallinity and molecular mass of polyolefins and impact strength is well documented in literature [11, 12]. To investigate the relationship between the impact properties and comonomer content of the propylene / 1-pentene random copolymers, only samples having similar molecular weights and different 1-pentene contents were considered. A subset of the polymers described and characterised in Chapter 6 was used for the evaluation. The set of samples, all with molecular weights around 420 000 g/mole, is listed in the table below.

Table 9.1: Subset of samples used to determine relationship between impact strength and comonomer content

Sample Nr.	1-Pentene (wt%)	Mw (g/mol)	Mn (g/mol)	MWD (Mw/Mn)	MFI (dg/min)
PP-2	0	440668	85277	5.2	7.4
COP-1	1.03	446923	85023	5.3	7.0
COP-2	1.97	415298	83278	5.1	7.0
COP-3	3.11	415608	76973	5.4	8.5
COP-4	4.04	406325	78432	5.3	8.0
COP-20	4.90	405880	76581	5.3	7.5

The notched Izod impact strength of these random copolymers are presented in Figure 9.7. It can be seen that impact strength increases with an increase in comonomer content in a linear fashion. The heats of fusion determined for a set of propylene / 1-pentene random copolymers and reported in Table 8.1 show that an inverse relationship between 1-pentene comonomer content and crystallinity exists. The resultant inverse relationship between impact strength and crystallinity as proposed by Van Schooten et. al. and Shearer et. al. is thus confirmed.

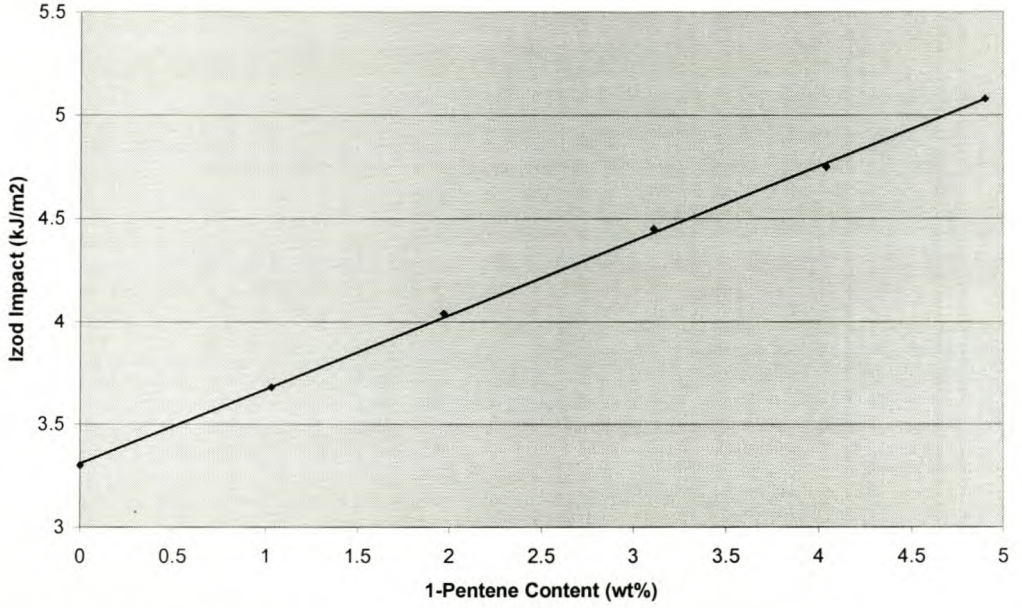

Figure 9.7: Izod impact strength as a function of comonomer content

It is also known that the average molecular weight has a significant effect on the impact strength of PP homopolymers [13]. In order to investigate the impact strength relationship of propylene / 1-pentene random copolymers with molecular weight, a series of copolymers with similar 1-pentene content and different molecular weights were considered. The subset of polymers, described and characterised in Chapter 6, is shown in Table 9.2 below.

Table 9.2: Subset of samples used to determine relationship between impact strength and molecular weight

Sample Nr.	1-Pentene (wt%)	Mw (g/mol)	Mn (g/mol)	MWD (Mw/Mn)	MFI (dg/min)
COP-5	3.9	268557	50210	5.3	40
COP-6	3.9	361761	67220	5.4	22
COP-21	3.5	665082	110997	6.0	6.0
COP-8	3.9	851702	137001	6.3	2.4

In Figure 9.8 the notched Izod impact strength of propylene / 1-pentene random copolymers with similar comonomer content is plotted against

molecular weight. The direct relationship between molecular weight and impact strength can be observed.

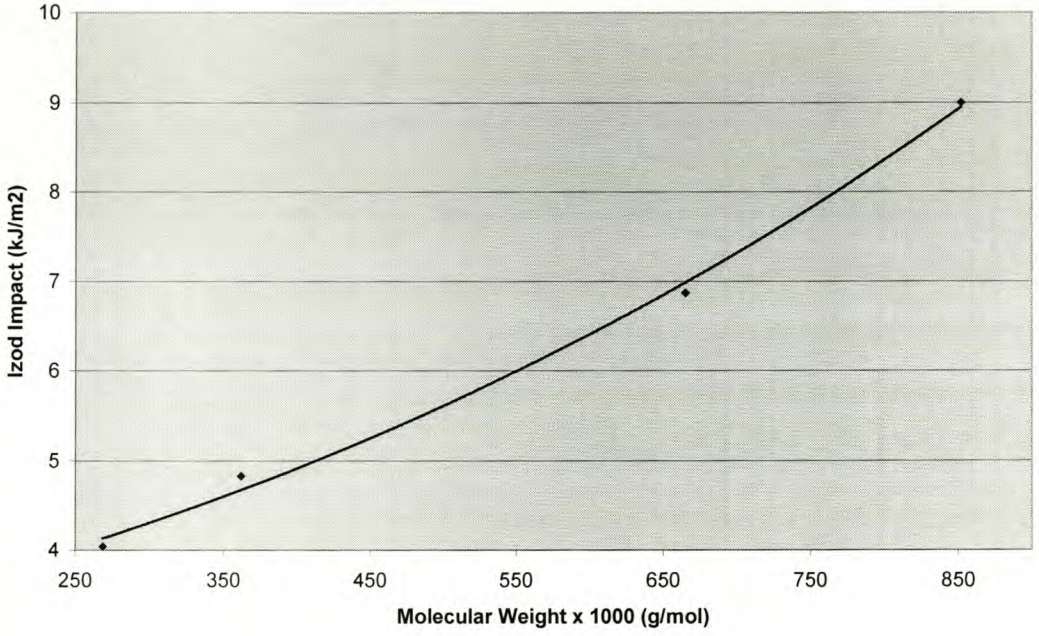

Figure 9.8: Izod impact strength as a function of molecular weight

9.3 OPTICAL PROPERTIES

Transparency could be a desirable property of polymers. The incorporation of small amounts of a comonomer into the polymer backbone and the addition of nucleating agents can improve the transparency of PP. Ethylene and to a lesser degree 1-butene, as mentioned earlier, are exclusively used as comonomers in the production of commercially available high clarity PP products.

According to the theory of Rayleigh the scattering of light, resulting in poor clarity, for semi-crystalline polymers can be attributed to the large density variations between the crystalline spherulites and amorphous regions [14]. Within spherulites and also between spherulites light beams must make many transitions between amorphous and crystalline phases resulting in scattering. However, the theory of Rayleigh is only applicable to particles smaller than the wavelength of light.

Debye and Beuche extended Rayleigh's theory to also account for particles larger than the wavelength of light [15]. They found that the primary source of light scattering in semi-crystalline polymers could be attributed to the interaction between visible light and spherulites larger than the wavelength of the light. Taking these factors into account Mount argued that the transparency of semi-crystalline polymers can be improved by [16]:

- Reducing the spherulite size
- Reduce the amorphous content
- Reducing the difference in density between amorphous and crystalline regions

The full set of results obtained from the transparency evaluations, as measured by UV/VIS spectroscopy at wavelengths between 350 and 850 nm, is given in Table 9.3 below. All the materials and analytical methods are described in Chapter 6.

Table 9.3: Transparencies of a series of propylene random copolymers with 1-pentene and ethylene as comonomers respectively, measured over a range of wavelengths

Sample nr.	Co-Monomer	Content (wt%)	Transparency at selected wavelengths					
			350 nm	450 nm	550 nm	650 nm	750 nm	850 nm
PP-2	-	-	54	60	64	67	69	71
COP-25	C5	0.63	60	63	68	70	73	75
COP-26	C5	0.96	62	64	69	71	73	75
COP-27	C5	2.0	62	64	69	71	73	75
COP-23	C5	5.9	64	67	72	74	76	78
COP-21	C5	3.5	66	68	74	76	77	79
COP-10	C2	2.5	56	61	65	68	71	73
COP-11	C2	3.5	58	63	67	70	72	76
COP-12	C2	5.0	59	63	67	70	72	76
COP-24	C2	3.5	60	64	67	70	72	74

All the random copolymers showed improved optical properties with increased comonomer content up to 3.5%. No optical benefits are obtained beyond 4.0 wt% incorporation of both ethylene and 1-pentene comonomers into the polymer backbone.

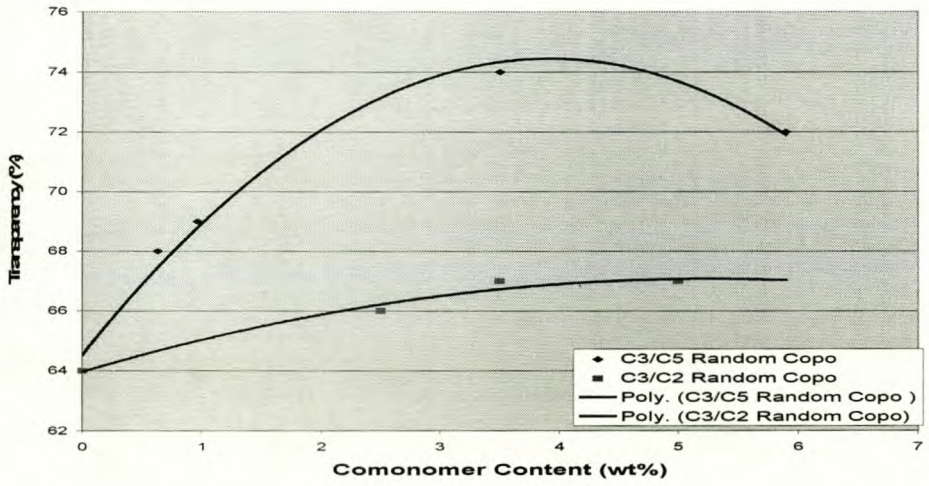

Figure 9.9: Transparencies of PP random copolymers with 3.5 wt% comonomer content measured at 550nm

The Transparency of propylene random copolymers with ethylene and 1-pentene as comonomers respectively, were compared over 350 nm to 850 nm wavelength range and the results presented as Figure 9.10. Random copolymers with similar MFR's and 3.5-wt% comonomer content were selected for evaluation. This can be rationalised by the higher degree of supercooling obtained with PP random copolymers employing 1-pentene as comonomer [17] as reported in Chapter 8.

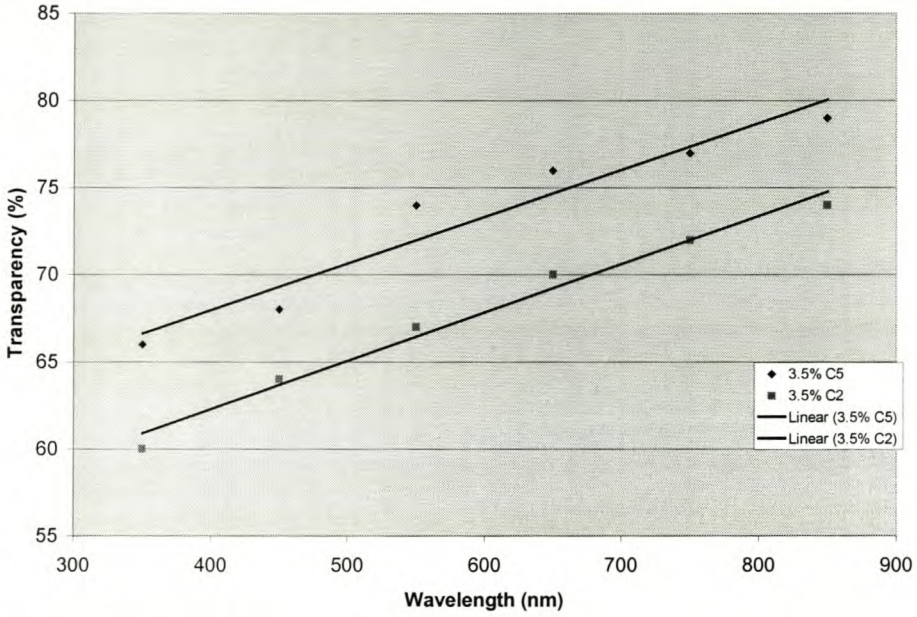

Figure 9.10: Transparency propylene random copolymers with 1-pentene and ethylene as comonomers respectively - both at 3.5 wt% content

9.4 DENSITY

The inverse relationship between density and comonomer content is described in literature [18]. Although the 1-pentene comonomer is not excluded from the crystal phase as reported earlier in section 8.3, it forms a defect in the crystal reducing the density of the crystalline phase. The crystallisation process is subject to two structural factors, namely [19]:

- Branch length
- Crystallisable propylene sequence length

A longer branch will naturally have a more pronounced effect on the size of the defect. However, crystallisation of these copolymers is also dependent on the branch distribution in the polymer backbone. A more random distribution will be more effective in reducing crystallinity.

The results obtained show that density (ρ) is directly related to 1-pentene content (P). For these random copolymers it was found to approximately comply with the equation $\rho = 0.0001P^2 - 0.005P + 0.908$.

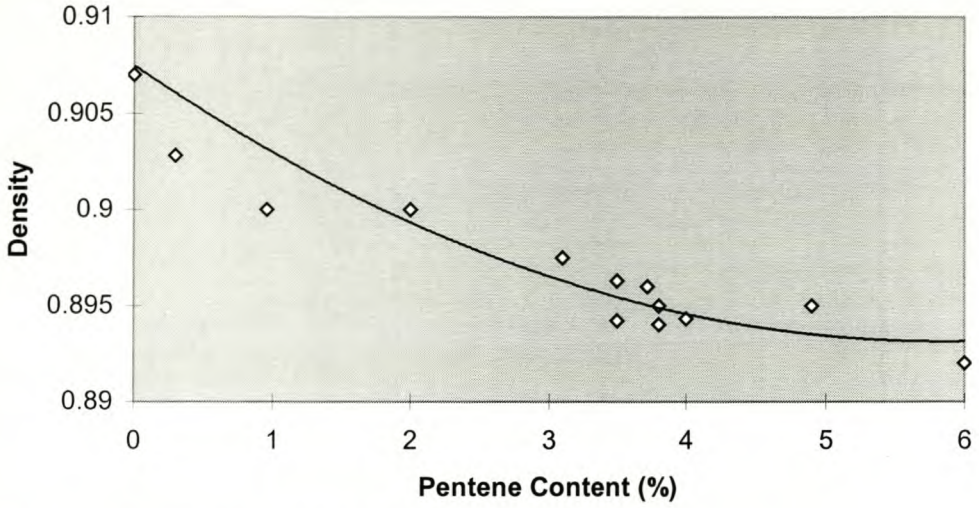

Figure 9.11: Density of C3 / C5 Random Copolymers

9.5 OTHER PHYSICAL PROPERTIES

For completeness sake a study was undertaken to determine the physical properties of propylene / 1-pentene random copolymers less frequently measured. The measured properties were compared to those of propylene / ethylene random copolymers and propylene homopolymer.

9.5.1 Characterisation materials and analytical methods used in the characterisation of comparative study of physical properties

- The 1-pentene content was determined on a Perkin Elmer FT-IR 1720X instrument on compression moulded film according to a method previously described.

- Ethylene content was determined by ^{13}C NMR on a Varian 400 MHz by scanning a solution of 0.4 g copolymer in 2 ml o-dichloro benzene at 120 °C using H_2SO_4 as external lock, a 90° pulse, a pulse width of 10,30 second relaxation delay and 2000 scans.

- The melt flow index (MFI) was determined according to ASTM D 1238.

- Density was measured according to ASTMD 1505.

- Crystallinity was determined from the fusion enthalpy measured by DSC. A Perkin Elmer DSC-4 equipped with an Intracooler II controlled by a TADS data station was used for the determination of the fusion enthalpy. The samples have been heated from 50 to 200°C at 20°C/min, held at 200°C for 1 minute, cooled to 50°C at a rate of 20°C/min and held for 1 min after which the analysis was recorded between 50 and 200°C at a heating rate of 10°C/min.

- Rheological measurements were made on a controlled stress Rheometric SR 500 dynamic rheometer.

The control set of materials used in the study is listed in the table below.

Table 9.4: Polymer Properties

Sample	Comonomer	Content (%)	MFI (dg/min.)	Density (g/cc)	Crystallinity (%)
1	Homo	0	1.5	0.9050	47.1
2	Ethylene	3	1.5	0.9010	37.5
3	1-Pentene	1.5	1.5	0.9033	45.1
4	1-Pentene	3	1.5	0.9018	43.2
5	1-Pentene	5.5	1.5	0.9001	39.7

9.5.2 Experimental

9.5.2.1 Characterisation method: Solvent absorption

Solubility behavior was determined by stirring 100.0g of ~8 mm^3 pellets in different polar and non-polar solvents at 23 °C for 20 days after which the solvent was decanted and the pellets dried in a stream of air at room temperature. The amount of solvent absorbed was determined by weighing. Pellets were then dried in a vacuum oven at 90 °C until a constant weight indicated that all solvent was removed.

The samples were again weighed to determine the amount of polymer extracted by the different solvents. The samples were also stirred for the same period of time in 30% Ammonia, 1 N chromic acid, 50% Potassium Hydroxide, 30% Sodium Hydroxide and 30% Sulfuric acid. The pellets were then washed, dried and inspected visually for color- or physical changes.

9.5.2.2 Characterisation method: Gas permeability

Gas permeability measurements were carried out on compression moulded film prepared from the samples of Table 9.4 using a Yanaco GTR-20 Gas Permeability Analyzer under the following conditions:

Temperature : 20°C

Humidity : 0%

Test gas : Mixture of 79.4% 0_2/ 20.6%$C0_2$
Carrier gas : He

Permeation area	:	15.2 cm^2
Gas pressure 0_2	:	82.18 cm Hg
Gas pressure $C0_2$	:	21.32 cm Hg
Film thickness	:	as per sample

9.5.2.3 Characterisation method: Dielectric constant

Dielectric properties were determined at room temperature using a Micromet Eumetric System III Dielectrometer with a mid conductivity interface. The 4 mm thick compression-moulded samples were placed between 10 mm diameter gold plated parallel electrodes pressing against the sample with a constant force of 200 mN. A voltage of 500 V at the different frequencies was applied at 20 second intervals.

9.5.2.4 Characterisation method: Thermal conductivity

Thermal conductivity measurements were done on a Lees' conductivity apparatus using 200 µm thick melt-pressed discs and after thermal equilibrium was established the conductivities were calculated using the following equations (CT):

$$e = VI/ (a_AT_A+a_s[T_A+T_B]/2+ a_BT_B+a_CT_C)J.s^{-1}.m^{-2}.{}^oC^{-1} \quad (1)$$

where e is the energy in joules emitted from each exposed area per second per °C above ambient, a_A, a_b, a_C and a_s are the exposed surface areas of discs A, B, C and the sample S in m^2. T_A, T_b, and T_C are the temperatures of discs A, B and C in °C at the steady state above ambient, the heat supplied by the heating element with V the potential difference across the heating element in volts and I is the current flowing measured in amperes.

Conductivity K can be calculated by:

$$K = ed (a_S[T_A+T_B]/2+ 2a_AT_A)/(2\pi r^2[T_B-T_A]J.s^{-1}.m^{-1}.{}^oC^{-1} \quad (2)$$

where d is the thickness and r is the radius of sample S.

9.5.2.5 Characterisation method: Linear thermal expansion

Linear thermal expansion was determined over the temperature range –20 to 40 °C on a Perkin Elmer DMA 7e with a 5 mm diameter probe and a constant force of 200 mN pressing down on the 4 mm thick injection-moulded samples.

The coefficient of linear thermal expansion (α) of a sample of thickness L_0 is calculated from the change in sample thickness ΔL over the temperature range ΔT employed according to equation 3.

$$\alpha = \triangle L/L_0 \ \triangle T \ ^oC^{-1} \ mm.mm^{-1}. \ ^oC^{-1} \quad (3)$$

9.5.3 Results and discussion

The results are presented in a set of tables below. All the results can be rationalised by the observed reduction in crystallinity and melting point.

9.5.3.1 Solvent absorption

Table 9.5: Solvent Absorption

Solvent	Sample				
	1 (mass%)	**2 (mass%)**	**3 (mass%)**	**4 (mass%)**	**5 (mass%)**
Acetone	1.5	1.67	1.9	2.1	2.7
Ethyl Acetate	5.3	5.4	5.7	5.6	5.7
Ethyl Alcohol	0.1	0.2	0.1	0.1	0.2
Ethylene Glycol	0	0	0	0	0
n-Heptane	13.1	10.5	13.8	14.5	16.5
Tetrahydofuran	14.4	12.8	16.1	15.2	18.5
Toluene	15.6	13.5	16.9	17.5	20.0
p-Xylene	16.0	12.9	15.9	16.2	19.5

9.5.3.2 Gas permeation

Table 9.6: Gas Permeability

Sample	**Film Thickness (µm)**	**0_2 Permeability ($P.10^{13}$ $cm^3.cm^{-2}.s^{-1}.Pa^{-1}$)**	**$C0_2$ Permeability ($P.10^{13}$ $cm^3.cm^{-2}.s^{-1}.Pa^{-1}$)**
1	45	1.29	4.25
2	50	1.33	4.37
3	40	1.29	4.29
4	50	1.33	4.34
5	45	1.59	4.70

9.5.3.3 Electric properties

Table 9.7: Electric Properties

Sample	**Dielectric Constant**	**Dissipation Factor**
1	2.15	0.004
2	2.19	0.005
3	2.25	0.003
4	2.31	0.005
5	2.50	0.003

9.5.3.4 Thermal conductivity

Table 9.8: Thermal Conductivity

Sample	**Thermal Conductivity ($J.s^{-1}.m^{-1}.°C^{-1}$)**
1	0.287
2	0.241
3	0.277
4	0.266
5	0.280

9.5.3.5 Linear thermal expansion

Table 9.9: Linear Thermal Expansion

Sample	**Tg(°C)**	**Coefficient of Linear Thermal Expansion ($a.10^5.°C^1$)**	
		-20°C to Tg	**Tg to 30°C**
1	-3	6.7	10.4
2	-2	6.1	10.8
3	-3	5.9	10.5
4	-3	5.8	11.1
5	-4	6.6	10.9

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CHAPTER 10

UP-SCALING THE GAS-PHASE PRODUCTION OF PROPYLENE / 1-PENTENE RANDOM COPOLYMERS FROM 10 LITRE BENCH-SCALE AUTOCLAVES TO AN 800 LITRE PILOT PLANT REACTOR TO A COMMERCIAL PLANT WITH A 50 M^3 REACTOR

10.1 INTRODUCTION

Following the successful gas-phase synthesis of propylene / 1-pentene random copolymers in 10 litre autoclaves and the exciting and unique range of rheological, thermal, mechanical and physical properties, in relation to commercially available PP random copolymers, obtained, a study was initiated to determine the feasibility of commercialising these polymers.

The feasibility study included carrying out a pilot-plant trial on an 800-liter reactor in Germany. The gas-phase pilot plant is a replica of Sasol's 50 m^3 Novolen gas-phase plant in Secunda, South Africa. During this two- week trial a range of propylene / 1-pentene random copolymers was produced. The 17 tons of material produced were analysed and used in a market acceptance study. The information obtained from the pilot-plant trial in combination with the results of computer simulations was used to plan the first production run on a world-scale 50 m^3 gas-phase plant. Modifications to the plant and the results from the commercial production run are discussed.

10.2 NTH GAS-PHASE PP PRODUCTION TECHNOLOGY

Development of the NTH vertically stirred bed gas-phase technology began within BASF in the year 1962 [1]. The first commercial unit, a homopolymer plant with reactor volume of 25 m^3 and output of about 2 tonnes per hour, was commissioned in 1967 and is still in operation today. For the production of homo-, random co- and ter-polymers a single reactor is employed whereas two reactors in cascade is required for the production of impact copolymers [2]. As the focus of this study is on the synthesis of random copolymers only the design and operation of the single reactor system, shown in Figure 1 below, is described and discussed.

The gas-phase processes provide an attractive environment for polyolefin polymerisation with no liquid inventory. However, to be competitive with liquid-phase processes, gas-phase reactors must operate close to the dew point of the monomer mixture to obtain high monomer concentrations and high catalyst yields [3].

The basic steps in this process are [1]:

- Polymerisation in the vertically stirred reactor vessel
- Discontinuous discharge of polymer powder from reactor
- Separation of polymer powder and unreacted monomers
- Extrusion and pelletisation

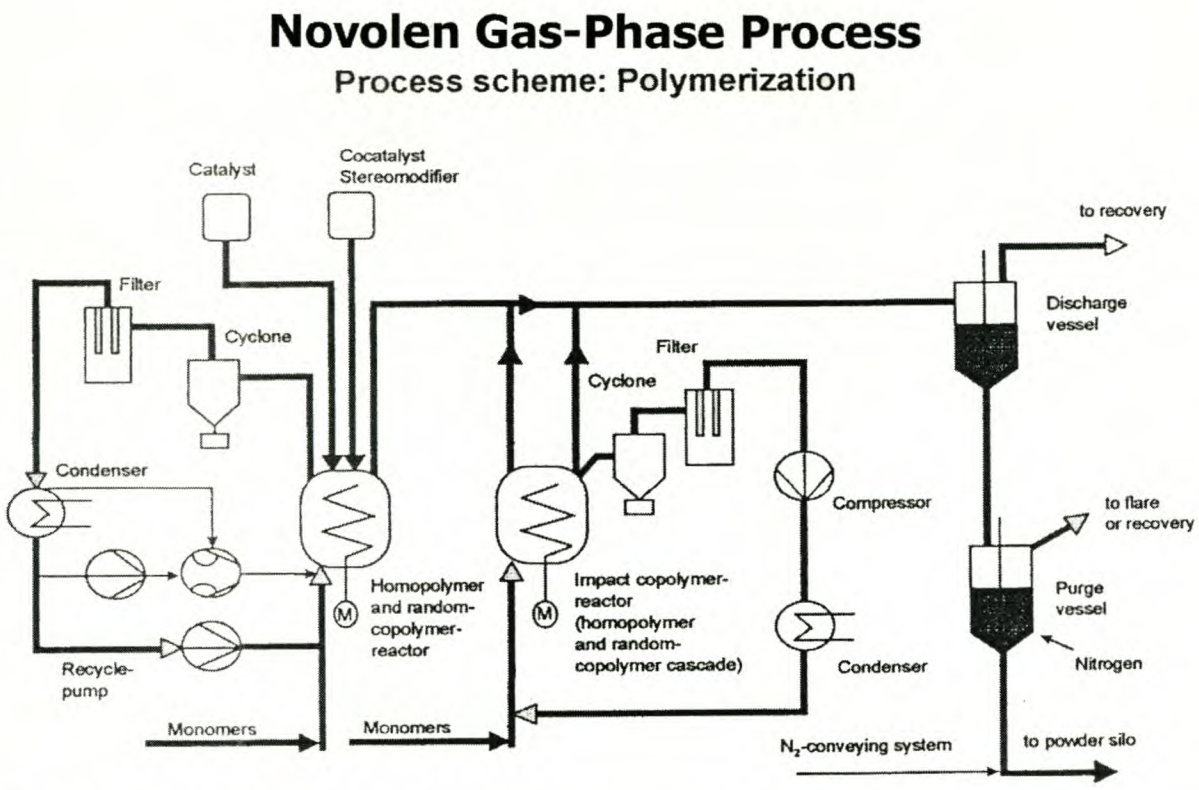

Figure 10.1: NTH's gas-phase vertically stirred bed PP production process

Catalyst, co-catalyst, stereo-modifier, hydrogen and monomer mixtures, in the required ratio, are fed to the reactor. Uniform conditions are maintained in the polymer bed by mechanical mixing using a helical agitator mounted at the bottom of the reactor. By using mechanical agitation rather than fluidisation to provide mixing, gas circulation is minimised.

The heat of evaporation of the liquid monomer is used to facilitate heat removal in the reactor, since the polymerisation process is exothermic. Gas from above the polymer powder bed is recycled and condensed before being re-introduced into the reactor [4]. Temperature in the reactor is controlled by the ratio of gas recycled to the polymer production rate.

A mixture of polymer powder, monomers and hydrogen is discharged from the reactor through a ball valve and dip tubes. Adjusting the length of pulse and / or frequency of the discharge valves controls the discharge rate, maintaining the bed height at a constant level. The polymer and carrier-gas are separated in the discharge vessel and the carrier gas, normally about 20%, is recycled.

10.3 MODELLING OF CRITICAL OPERATIONAL CONDITIONS

10.3.1 Condensation point calculations

The dew points of typical gas mixtures for random copolymerisation of propylene and 1-pentene were determined and the range of safe operating conditions defined in Chapter 5. It was found that the same operating

conditions used during the production of propylene / ethylene random copolymers could be employed when introducing 1-pentene as comonomer.

10.3.2 AspenPlus process simulation

A process flow diagram of the Novolen gas phase was developed in AspenPlus. The results of different simulation runs using ethylene and 1-pentene respectively, as comonomer during the production of propylene random copolymers were then compared.

In order to calculate the composition and flow rates of recycle streams and reactor discharge a base set of assumptions were made in order to develop a mass balance over the reactor. The set of assumptions is shown in Table 10.1 below.

Table 10.1: List of assumptions made

	Assumptions		
1	The carrier gas exiting the reactor is 18 $\%^{mass}$ of the fresh propylene feed flowrate		
2	81 $\%^{mass}$ of the hydrogen feed does not react (from current data on the reactor)		
3	3.2 $\%^{vol}$ of the carrier gas exiting the reactor is 1-pentene (measured value from pilot plant trial)		
4	3.0 $\%^{mass}$ of the polypropylene is 1-pentene (same as the ethylene content)		
5	The composition of the propylene feed is :	Propylene	0.989
		Propane	0.010
		Ethane	0.001
6	The 1-pentene feed was assumed to contain only 1-pentene		

Using the same set of assumptions regarding specifications of condenser dimensions and cooling water inlet temperature and flow rate, the condensing capacity (duty) of the heat exchanger, for the ethylene and 1-pentene rich recycle streams respectively, was calculated using the heat exchange design programme HTFS (MTASC). The AspenPlus software tool from AspenTech was used to predict the thermodynamic properties of the respective recycle streams. Typical gas compositions for ethylene and 1-pentene rich recycle streams found during the production of random copolymers with a 3 wt% comonomer content were calculated and used in the simulations.

The simulation results, tabulated below, show a 20% increase in the condensable mass flow rate for the 1-pentene rich recycle stream compared to the flow rate obtainable with the ethylene rich recycle stream. Using this as a basis to calculate the duty of the condensers and by taking the heat of

reaction for the respective comonomers into consideration, this translates to a 13% increase in the potential throughput of the reactor.

Table 10.2: Mass flow rates and duties of the heat exchanger for both ethylene and 1-pentene copolymerisation scenarios

Case 1 : Ethylene : C_2/C_3 (polymer) = 3%mass	Recycle Flow, kg/hr	81061
	Duty, kW	7764
	Product produced, t/h	11.172
Case 2 : 1-Pentene C_5/C_3 (polymer) = 3%mass	Recycle Flow, kg/hr	98000
	Duty, kW	8546
	Product produced, t/h	12.628
Differences	Throughput	13 %
Reaction Energies	Ethylene, KJ/kg	3334
	Propylene, KJ/kg	2476
	Pentene, KJ/kg	1148

The carrier gas from the reactor is condensed before being returned to the purification plant. The use of 1-pentene as comonomer had no detrimental influence on the compression process in the carrier gas compressor. No condensation occurred between the stages of the carrier gas compressor. The simulation results also showed that the distillation columns of the purification plant, with ethylene and 1-pentene as comonomer respectively, performed almost identically.

10.4 PILOT PLANT TRIALS

10.4.1 Experimental

Five reactor grades of propylene / 1-pentene random copolymers were produced on BASF's 800 litre stirred bed continuous gas-phase pilot plant reactor. This pilot plant was selected as it is nearly identical to Sasol's Novolen plant in Secunda, South Africa. The 1-pentene content of the random copolymers produced ranged from 1.2 to 5.7 wt%.

Sasol supplied the polymerisation grade 1-pentene in $1m^3$ IBC containers. The containers were connected to the comonomer support unit and fed to the reactor through drying columns packed with molecular sieves. A typical fourth generation supported Ziegler-Natta catalyst (PTK4WSG) was used in

combination with a triethylaluminium (TEA) co-catalyst. During the first 2 production runs a different external donor (silane) was employed to that used for production of the remaining 3 grades.

The only significant change made to the polymerisation process was to increase the temperature of the discharge vessel to 80°C to ensure the effective separation of residual monomer from the polymer powder. The process conditions used during the production of the 5 reactor grades are recorded in Table 10.3 below.

Table 10.3: Pilot plant trial: Process conditions

Trial no.	**B2116**	**B2117**	**B2118**	**B2119**	**B2120**
Catalyst	PTK4WSG	PTK4WSG	PTK4WSG	PTK4WSG	PTK4WSG
Silane	CPMS	CPMS	BUPS	BUPS	BUPS
Reaction conditions					
Temperature (°C)	80	80	80	80	85
Pressure (bar)	32	23	23	23	20
C_3 (kg/h) fresh feed	188	166	170	175	174
Recycle gas feed point: Top / bottom of reactor (kg)	203 / 507	196 /453	201 / 448	200 / 451	211 / 401
H_2 (volume %)	0.74 (230l/h)	0.77 (98.7l/h)	0,1 (261l/h)	0.13 (301l/h)	0.12 (321l/h)
C_5 (volume %)	1.7 (8.4kg/h)	3.5 (15.0kg/h)	1.4 (3.7kg/h)	3.1 (12kg/h)	6.0 (15.2kg/h)
TEA (1M) (ml/h)	450	450	450	450	450
Silane (0.25M) (ml/h)	180	180	180	180	180
TEA : Silane ratio (mol/mol)	10:1	10:1	10:1	10:1	10:1
Throughput rate (kg/h)	155	151	150	150	150
Carrier gas (%)	20.5	16.7	13.7	19.6	20.5
Reactor residence time (h)	1.6.	1.6	1.6	1.6	1.6

The polymer powder was stabilised during the extrusion process and pelletised. The polymer was analysed with regard to the properties listed below using similar techniques as described in Chapter 6:

- Thermal properties
- Melt Flow Ratio
- Molecular weight and distribution
- Comonomer content
- Tensile modulus
- Flexural modulus
- Catalyst productivity
- Powder morphology

10.4.2 Results and discussion

The 5 batches of polymer produced, with a 1-pentene comonomer content ranging between 1.2 and 5.7%, were characterised with regard to the set of properties mentioned in the paragraph above. The full set of results is given in Table 10.4 below.

Table 10.4: Pilot plant trial: Results of product characterisation

Trial no.	B2116	B2117	B2118	B2119	B2120
General					
MFR (g/10 min)	2.3	2.9	1.2	1.3	1.4
Xylene solubles (%)	1.2	2.0	2.1	3.0	3.7
R2/1	8.9	13.3	9.1	13.4	16.4
Termal analysis					
Tm_1 (°C)	152.3.	138.6	151.1	138.5	128.5
ΔH_1 (J/g)	87	78	87	71	82
Tc_{onset} (°C)	116	110	128	107	101
Tc_{peak} (°C)	100.1	90.9	117.9	87.6	82.8
Tm_2 (°C)	152.2	145.8	153.7	144.2	139.4
ΔH_2 (J/g)	94	81	96	81	75
Molecular characteristics					
C5 content (wt%) (NMR)	1.5	4.0	1.2	3.8	5.7
Mw (weight average)	418781	372611	527806	518432	481483
Mn (number average)	111840	107894	135620	147812	133648
Mol. Weight Dist. = Mw/Mn	3.74	3.50	3.89	3.49	3.60
Catalyst activity					
Cl value [ppm]	23	19	46	34	32
Catalyst Yield (gPP/gcat]	13130	15890	6565	8970	9530
Mechanical properties					
Flexural Modulus	597	413	582	401	327
Tensile Modulus	1348	998	1384	1012	648
Powder Morphology					
Powder density (g/l)	457	450	433	470	417
Flow property: R20 (g/sec}	58.8	52.6	50.0	58.8	50.0
d' (average) [mm]	0.8	1.0	0.8	O.9	1.0
Particle size distribution:					
<0,125mm [%]	4.2	2.0	4.2	3.5	0.2
<0.25mm [%]	6.6	4.9	6.0	5.9	1.4
<0.50mm [%]	18.5	16.0	22.5	17.5	12.2
<1.0mm [%]	46.0	42.4	51.1	47.1	53.3
<2.0mm [%]	25.0	32.7	15.8	25.5	32.4
>2.0mm [%]	0.3	2.1	0.3	0.5	0.6

Several interesting observations were made during the production trial runs and product characterisation. These are discussed in more detail below.

10.4.2.1 Polymer characterisation

The 1-pentene comonomer content of the random copolymers produced ranged between 1.2 and 5.7%. The degree of polymerisation could effectively be controlled by the chain transfer agent (H_2) and the monomer molar ratio in the reactor had no visible influence on the molecular weight distribution. The differential between peak melting point and heat of fusion of the powder (Tm1, ΔH_1) and the recrystallined material (Tm2, ΔH_2) respectively, is typical. The onset of crystallisation and peak crystallisation temperature (cooling rate of 20°C, from above the melt temperature at 210°C) as well as the melting point depression is similar to that obtained for the propylene / 1-pentene random copolymers produced in 10l autoclaves as described in Chapter 8.

The R21 values listed is determined by ^{13}C NMR and are related to the atactic content in PP polymers. This relatively simple and quick analytical technique is used by plant operators to predict (control) the comonomer content during the production of PP copolymers.

10.4.2.2 Catalyst activity

The residual chlorine (Cl) content in the polymer is used to determine the catalyst yield. A dramatic increase in catalyst activity was observed with increasing 1-pentene to propylene monomer feed ratio for both external donors used. This confirms the results of the kinetic study conducted in 10l bench-scale autoclaves as reported in Chapter 6. In the range of 1.2 to 4% 1-pentene comonomer content random copolymer an increase in catalyst activity of about 8% per 1% increase in comonomer content was observed for both the external donors employed.

10.4.2.3 Reactor behaviour

Excellent reactor stability was achieved during the production of 1-pentene copolymers. No condensation (evident by the formation of lumps in the reactor) was observed at the process conditions used during the trials. The reactor temperature and pressure ranged between 80 and 85°C and between 32 and 20 bar respectively during the production of propylene / 1-pentene random copolymers with comonomer content ranging between 1.2 and 5.7%. The reactor throughput was not limited by the monomer molar ratio in the reactor.

10.4.2.4 Powder morphology

The particle size distribution is of critical importance to operations down-stream of the reactor with large particles (>5mm = giants) blocking valves and transfer lines. The particle size distribution also has a direct influence on the powder flowability and density with a reduction in the average particle size (diameter) and size distribution both improving flowability and density.

The powder morphology during the gas-phase production of propylene / ethylene random copolymers is very sensitive to the reactor and ethylene partial pressure. To prevent the formation of giants reactor pressure during the production of propylene / ethylene random copolymers is controlled around 17 bar and comonomer content (wt%) restricted to a range of between 0 and 3.5%.

The morphology of the reactor powder obtained during the production of propylene / 1-pentene random copolymers showed a narrow distribution and good average particle size. No obvious relationship between powder morphology and reactor and 1-pentene partial pressure was observed. This presents a huge benefit as the rate of polymerisation is directly related to monomer concentration, which in turn is related to the reactor pressure [5, 6].

10.4.2.5 Other general observations

- The removal of residual monomer from the product was highly effective by operating the discharge vessel at 80°C.
- The propylene / 1-pentene random copolymers were noticeably less sticky than ethylene copolymers with similar comonomer content (%mass).
- The extremely low Xylene Soluble (XS) content for random copolymers with a relative high comonomer content obtained. This is a huge advantage in food applications where a low melting point is required.

10.5 PRODUCTION ON 50 m^3 COMMERCIAL PLANT

10.5.1 Introduction

The 17 tonnes of material produced during the pilot plant trial at BASF in Ludwigshafen, Germany, was shipped to South Africa and used in an application and market acceptance study. The positive results obtained from this study, reported on in Chapter 11, in combination with the successful pilot plant trial prompted the decision to commercialise the production of propylene / 1-pentene random copolymers. This section describes the results from the first production run on Sasol's 50 m^3 Novolen gas-phase plant.

10.5.2 Experimental

For the first production run a temporary reservoir and feed system for the 1-pentene had to be installed. A set of four 25 m^3 iso-containers was used as 1-pentene reservoir. In addition to the iso-containers the installed system included a temporary pipe network, a diaphragm pump, corriolis flow meter reactor tie-in to the silane nozzle on top of the reactor. The pump was sized to deliver a maximum of 1000 kg/h (1850 l/h) of 1-pentene at a pressure of 35 bar. The pump operates on an automatic stroke adjustment to allow the ratio controller to adjust the 1-pentene flow rate. A schematic drawing of the 1-pentene dosing system is shown in Figure 10.2 below.

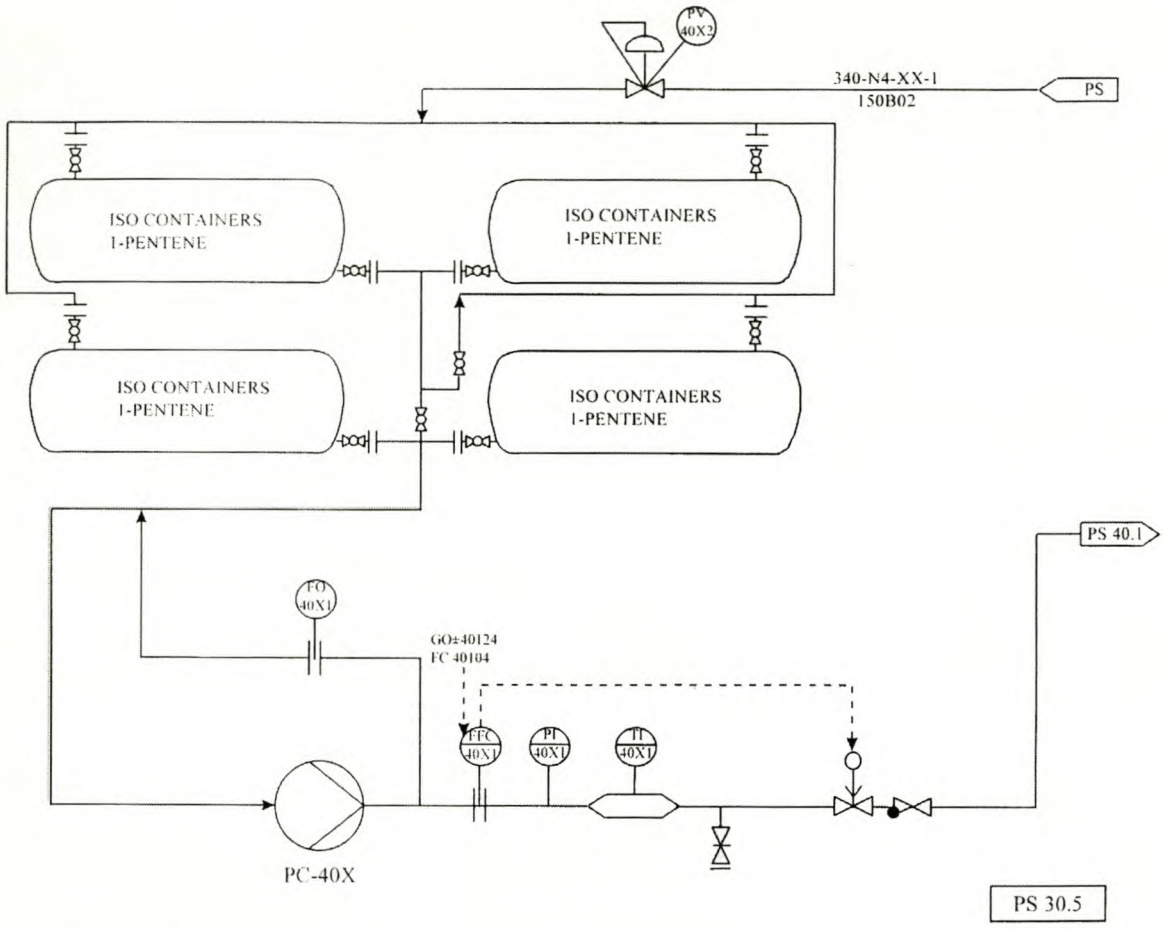

Figure 10.2: Temporary 1-pentene dosing system

The trial run was started from a typical homopolymer grade, with a MFR of 12, in the single reactor production line. The reactor operating pressure was reduced to 25 bar and the temperature maintained at 80°C. A 1-pentene flow rate of 250 – 450 kg/h was selected in tandem with a propylene feed rate of 11 t/h. The silane dosing point was changed to the bottom feed point to accommodate the feeding of the 1-pentene monomer from the silane dosing point on top of the reactor. The cascade loop controlling the propylene / 1-pentene monomer feed was subsequently activated. The fresh propylene feed was increased to 16 t/h over a period of 2 hours with the 1-pentene flow being adjusted automatically by the ratio controller. The hydrogen ratio was adjusted until the required MFR of 1.0 was reached.

Three propylene / 1-pentene random copolymer reactor grades were produced with comonomer contents of 1.7, 3.2 and 5.7% respectively. The reactor conditions that were maintained during the production of the 3 random copolymers can be obtained from Table 10.5 below. 160 Tonnes of material were produced of each of the copolymer grades with comonomer contents of 1.7 and 3.3% respectively and 40 tonnes of polymer with a comonomer content of 5.7%.

Table 10.5: Reactor Conditions

		1,5-wt% C5		3-wt% C5		5-wt% C5	
		BASF Pilot Plant	Sasol Novolen Plant	BASF Pilot Plant	Sasol Novolen Plant	BASF Pilot Plant	Sasol Novolen Plant
		0,8 m^3	**50 m^3**	**0,8 m^3**	**50 m^3**	**0,8 m^3**	**50 m^3**
Grade no.		B2218	5100	B2119	5200	B2120	5300
Catalyst		PTK4WSG	PTK4WSG	PTK4WSG	PTK4WSG	PTK4WSG	PTK4WSG
Silane		BUPS (0,25M, C7)	BUPS (7,5wt%, C7)	BUPS (0,25M, C7)	BUPS (7,5wt%, C7)	BUPS	BUPS (7,5wt%, C7)
		top, recycle gas	top, recycle gas	top, recycle gas	top, recycle gas	top, recycle gas	top, recycle gas
Alkyl		TEA (1M, C7)	TEA (100%)	TEA (1M, C7)	TEA (100%)	TEA (1M, C7)	TEA (100%)
		top, recyle gas	top, dome	top, recyle gas	top, dome	top, recyle gas	top, dome
Pentene		1 m3 IBC container	25 m3 container	1 m3 IBC container	25 m3 container	1 m3 IBC container	25 m3 container
		top, recycle gas	bottom, recyle gas	top, recycle gas	bottom, recyle gas	top, recycle gas	bottom, recyle gas
Reactor Conditions							
p / T	[bar] / [°C]	23 / 80	25 / 80	23 / 80	23 / 80	20/85	23/83
C_3 to catalyst	[kg/h]	170,1 kg/h	1,52 to/h	175,1 kg/h	1,52 to/h	174 kg/h	1,52 to/h
C_3 - Fresh	[kg/h]	n. r.	14,5 to/h	n.r.	11.0 to/h	n.r.	8,5 to
Recycle Gas	top/bottom[kg]	450 / 200 kg/h	66 / 26 to/h	450 / 200 kg/h	48 / 24 to/h	400 / 200 kg/h	29 / 6 to/h
H_2	[Vol-%]	0,1 (26l/h)	2,0 (580 g/h)	0,13 (30l/h)	1,0 (451 g/h)	0.12 (32l/h)	0,9 (349 kg/h)
C_5	[Vol-%]	1,4 (3,7kg/h)	1,3 (495 kg/h)	3,1 (12kg/h)	2,0 (682 kg/h	6,0 (15,2kg/h)	? (850 kg/h)
C_5/C_3 Ratio	[kg/to]	22	31	69	55	87	83
TEA		450 ml/h	3,48 kg/h	450 ml/h	2,64 kg/h	450 ml/h	2,04 Kg/h
TEA/C_3 Ratio	[kg/to]	0.30	0.22	0.30	0.21	0.30	0.20
BUPS		180 ml/h	7,25 kg/h	180 ml/h	5,5 kg/h	180 ml/h	4,25 kg/h
BUPS/C_3 Ratio	[g/to]	50	34	49	33	49	32
TEA:BUPS	[mol/mol]	10,0 : 1	10,0 : 1	10,0 : 1	10,0 : 1	10,0 : 1	10,0 : 1
Output		150 kg/h	11,5 to/h	150,4 kg/h	8,7 to/h	150,4 kg/h	6,7 to/h
Carrier Gas	[%]	13.7	21.0	19.6	21.0	20.5	21.0
ResidenceTime	[h]	1.6	1.2	1.6	1.6	1.6	2.1

10.5.3 Results and discussion

Table 10.5 presents a comparison on the reactor conditions of the pilot plant and commercial plant respectively to produce random copolymers with similar MFR's and 1-pentene comonomer contents. A comparison of the required feed ratios for the pilot and commercial plants respectively, to produce random copolymers with similar comonomer contents is shown in Figure 10.3.

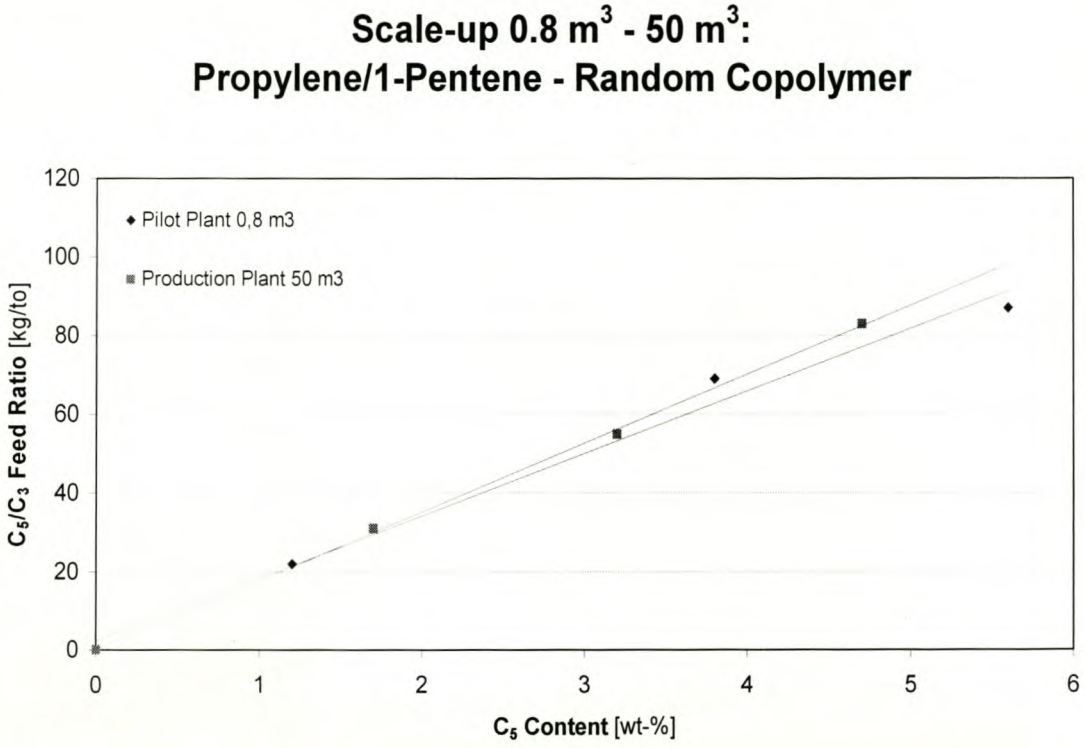

Figure 10.3: Comonomer feed ratios versus polymer comonomer content

Excellent reactor stability was experienced during the production run with very consistent MFR and R21 values. The introduction of pentene as comonomer into the reactor also had a positive influence on the control of the reactor temperature. The reactor throughput was constrained by the limited capacity of the 1-pentene pump.

The full set of results on product characterisation and powder morphology is presented in Table 10.6 below. The results are compared to those obtained from the pilot plant trial. Catalyst productivity achieved in the production plant is much higher than the productivity obtained during the pilot plant trial. The powder morphology, in line with the results obtained from the pilot run, was excellent with low amounts of fines (< 2mm) and giants (> 5mm) being produced.

Table 10.6: Product data of material produced on Sasol's plant

		1,5-wt% C5		*3-wt% C5*		*5-wt% C5*	
		BASF Pilot Plant	Sasol Novolen Plant	BASF Pilot Plant	Sasol Novolen Plant	BASF Pilot Plant	Sasol Novolen Plant
		0,8 m^3	**50 m^3**	**0,8 m^3**	**50 m^3**	**0,8 m^3**	**50 m^3**
Grade no.		B2218	5100	B2119	5200	B2120	5300
Product Data							
MFI	[g/10min]	1.2	1.2	1.3	1.0	1.4	1.1
R21		9.1	11.8	13.4	14.2	16.4	17.5
DSC (Tm_2)	[°C]	153.7	154.4	144.2	144.5	139.4	139.7
C_5 Content	[wt-%] (NMR)	1.2	1.7	3.8	3.2	5.7	4.7
Cl Value	[ppm]	46.0	16.0	34.0	16.0	32.0	20.0
Cat. Produktivity	[gPP/gKat]	6565	18750	8970	18750	9530	15000
Morphology							
Powder Density	[g/l]	433		470		417	
Flow Property: R20	[g/sec]	50.0		58.8		50.0	
d'	[mm]	0.8		0.9		1.0	
<0,125 mm	[%]	4.2	5.2	3.5	2.6	0.2	
<0,25 mm	[%]	6.0	8,2	5.9	6.1	1.4	
<0,50 mm	[%]	22.5	21,0	17.5	16.3	12.2	
<1,0 mm	[%]	51.1	36.2	47.1	32.6	53.3	
<2,0 mm	[%]	15.8	33.5	25.5	41.3	32.4	
>2,0 mm	[%]	0.3	0,9	0.5	1.1	0.6	

10.5.4 Summary of Process Advantages / Disadvantages

Table 10.7 summarises the process advantages and disadvantages obtained when replacing ethylene with 1-pentene as comonomer during the production of propylene random copolymers.

Table 10.7: Evaluation of Process Advantages / Disadvantages with the use of 1-pentene as comonomer for the production of random copolymers

	Advantages	Disadvantages
Recycle gas condenser	20% Increased cooling capacity	
Reactor throughput	13% Increased throughput	
Reactor stability	1-Pentene less reactive than ethylene	
Ejector (non-condensables)	Reduced load	
Monomer Cost		1-Pentene more expensive than ethylene
Carrier gas	Easy separation of propylene and 1-pentene in carrier gas stream	
Catalyst activity	Higher catalyst productivity for polymers up to 4wt% comonomer content	
Load on extruders	Reduced – due to the higher shear and temperature sensitivity as reported in Chapter 7.	
Powder morphology	Improve particle size and distribution obtained	
Stickiness	Less sticky than ethylene copolymers	

10.6 CONCLUSION

Propylene / 1-pentene random copolymers were successfully produced in the gas-phase on both the BASF 800l pilot plant and consequently on Sasol's 50 m3 Novolen plant. The introduction of 1-pentene as comonomer for the production of high clarity PP random copolymers offers a number of process advantages over the use of ethylene as comonomer. The main benefits obtained were improved powder morphology and reactor stability in combination with increased catalyst productivity and condenser cooling capacity.

These process advantages in combination with the premium in product properties achieved makes the use of 1-pentene as comonomer in the production of PP random copolymers a very attractive option.

Excellent correlation was obtained between the reactor conditions on BASF's 800l pilot plant and those on Sasol's 50 m^3 production plant during the production trials.

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CHAPTER 11

STABILISATION, NUCLEATION AND APPLICATION STUDY OF PROPYLENE / 1-PENTENE RANDOM COPOLYMERS

11.1 INTRODUCTION

Potential applications identified for the new family of propylene / 1-pentene random copolymers are in the following areas:

- The film market – cast, blown and BOPP films
- Injection moulding
- Blow moulding, and
- Thermoforming.

However, prior to using these new random copolymers in various applications, their stabilisation and nucleation had to be considered.

The stabilisation of PP can be considered as a matter of proper management of radical products or potential radicals by using the correct additives [1]. There are numerous stabilisers commercially available which provide the needed protection. Three main categories of stabilisers can be identified, namely:

- Primary antioxidants – interrupt the oxidisation cycle by reacting with formed radicals (radical scavengers)
- Secondary antioxidants – prevent new oxidisation cycles by decomposing hydro-peroxides
- Ultraviolet (UV) stabilisers – absorb energy of UV radiation

The presence of other additives such as flame-retardants and fillers in most cases cause a decrease in polymer stability.

Another type of additive is nucleating agents. The addition of nucleating agents to PP polymers leads to the modification of its crystalline structure, i.e. the reduction in spherulite diameter with the consequent changes in mechanical and optical properties. Regardless of what effect is required, it is brought about by the same mechanism: increased nucleation of the crystallising PP. Commercially available nucleating agents can be termed 'melt-sensitive' or 'melt insensitive'. The former has a melting point that is below or near the normal processing temperature of PP. They provide PP with enhanced clarity and lead to improved physical properties. These compounds are limited by their thermal decomposition at increased processing temperature [2].

To facilitate the commercialisation of the new family of propylene / 1-pentene random copolymers, therefore, a stabilisation study had to be conducted. The effectiveness of commercially available nucleating agents and optimum loading had to be determined.

11.2 STABILISATION

11.2.1 Introduction

In semi-crystalline polyolefins, including PP, a decrease in crystallinity is expected as the chain regularity is decreased by the random introduction of comonomer units. In Figure 11.1 the relative crystallinity of propylene / 1-pentene random copolymers is plotted against the 1-pentene content in the polymer. A value of 8.7 kJ/mole was used as the fusion enthalpy of 100% crystalline isotactic PP [3].

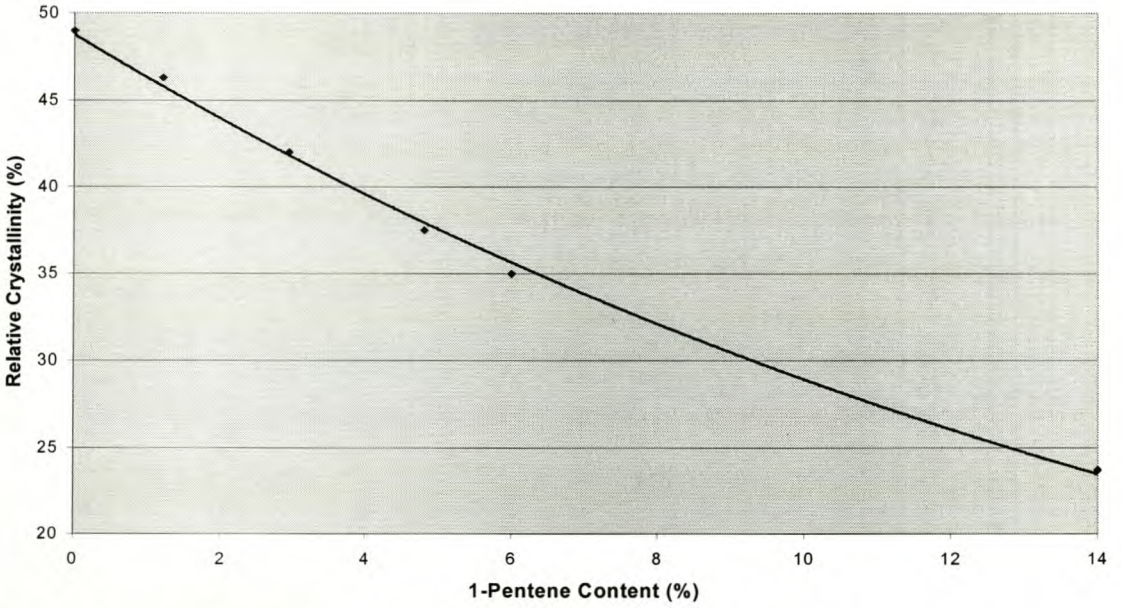

Figure 11.1 Crystallinity as a function of 1-pentene content

Certain short-range deformation properties of semi-crystalline high polymers have been found principally to be functions of the degree of crystallinity [4]. A decrease in crystallinity therefore contributes to improved application properties of propylene/1-pentene copolymers. However, it is also known that decreased crystallinity increases oxygen absorption [5] and consequently decreases the thermo-oxidative stability.

Most of the thermo-oxidative degradation mechanisms proposed for polypropylenes are based on the oxidation mechanism proposed by Bolland and Gee [6]. The chemical changes accompanying thermal oxidation of PP may lead to the formation of aldehydes, ketones, carboxylic acids and esters. The tertiary hydrogen is most susceptible to oxygen attack [7] and it was also previously reported that branching increases susceptibility to oxidation [8]. During a study of the degradation of propylene /1- pentene copolymers by multiple extrusion, the appearance of a carbonyl peak was observed at 1723 cm^{-1}. The peak height increased with processing temperature and thus it could be concluded that the degeneration rate of PP is temperature dependent.

According to Flory's theory of melting, the melting temperature of random copolymers will be depressed with increasing comonomer content as irregularities cannot be accommodated in the crystalline lattice. The decrease in melting temperature of propylene / 1-pentene random copolymers with increasing comonomer content is shown in Figure 11.2 below. Here propylene / 1-pentene random copolymers present an advantage since the processing temperatures of these copolymers are lower than that of the PP homopolymer.

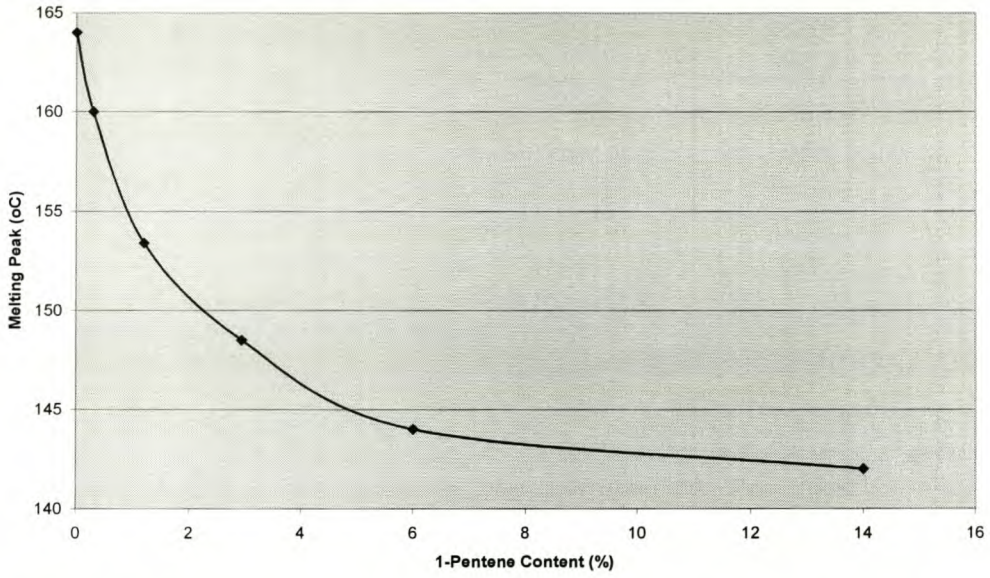

Figure 11.2 Decrease in melting temperature with 1-pentene content.

PP polymers are very sensitive to oxidative degradation and cannot be used without adequate stabilisation. A substantial amount of research was done in the field of PP stabilisation, but no information is available in the open literature about the degradation and stabilisation of propylene / 1-pentene copolymers. Decreased crystallinity of these polymers with increasing 1-pentene content increases their sensitivity to oxidation.

The degradation behaviour of propylene / 1-pentene random copolymers is investigated and the performance of a typical combination antioxidant package, at normal loading, evaluated.

11.2.2 Stabilisation studies

11.2.2.1 Sample preparation and stabilisation

PP polymers produced during the pilot plant trials in Germany supplemented by 4 commercial PP grades (2 homopolymers and 2 propylene / ethylene random copolymers manufactured on Sasol's Novolen plant) were used in the stabilisation, nucleation and application studies discussed in this chapter.

All the polymers used in the study were stabilised with a classical antioxidant package obtained from Ciba Speciality Chemicals, namely:

- 1000 ppm Ca-Stearate
- 600 ppm Irganox 1010 (tetrakismethylene(3,5-di-tert-butyl-4-hydroxyhydrocinnamate) methane)
- 500 ppm Irgafos PEPQ (tris(2,4-di-tert-butylphenyl) phosphite)

The synergistic effect obtained for a combination of primary and secondary antioxidants is well known [9].

Millad 3988 (3,4-dimethyl dibenzylidene sorbitol), obtained from Milliken Chemical Company was used in the nucleation studies, and if not otherwise specified, at a loading level of 2200 ppm.

To confirm loading levels of the classical antioxidants used, a previously described HPLC method was adapted [10]. Samples were extracted with chloroform in a soxhlet apparatus for 12 hours. Any extracted polymer was precipitated with methanol and the clear filtrate injected into a Hewlett Packard 1096 HPLC system equipped with a diode array detector.

Table 11.1 Description of samples used in stabilisation, nucleation and application study

Sample	Co-monomer	Content of Co-monomer	MFI	Nucleated	Description
1	-	0	40	Yes	Sasol 1145TC
2	-	0	2	No	Sasol 1102H
3	C_2	3	2	Yes	Sasol 3250H
4	C_2	3	12	Yes	Sasol 3250NC
5	-	0	1.4	Yes	Homopolymer B2108
6	C_2	2.1	1.2	Yes	C2 random copolymer B2109
7	C_2	2.8	3.2	Yes	C2 random copolymer B2105
8	C_5	1.2	1.5	No/Yes	C5 random copolymer B2118
9	C_5	1.5	7.5	Yes	C5 random copolymer B2116
10	C_5	1.2	12.5	Yes	C5 random copolymer. B2118
11	C_5	3.8	1.5	No/Yes	C5 random copolymer B2119
12	C_5	3.8	1.5	No/Yes	C5 random copolymer B2119
13	C_5	3.8	12.5	Yes	C5 random copolymer B2119
14	C_5	4.0	45	Yes	C5 random copolymer B2117
15	C_5	5.7	1.5	No/Yes	C5 random copolymer B2120

11.2.2.2 Measurement of degradation of multiple passes through an extruder

The degradation susceptibility of an unstabilised propylene / 1-pentene random copolymer with a comonomer content of 3.5% and MFR of 1.5 was illustrated by the increase in MFR with multiple extrusions and is presented for a range of extruder

temperature profiles. The outstanding behaviour of the propylene / 1-pentene random copolymer at the two lower temperature profiles can be observed in the figure below.

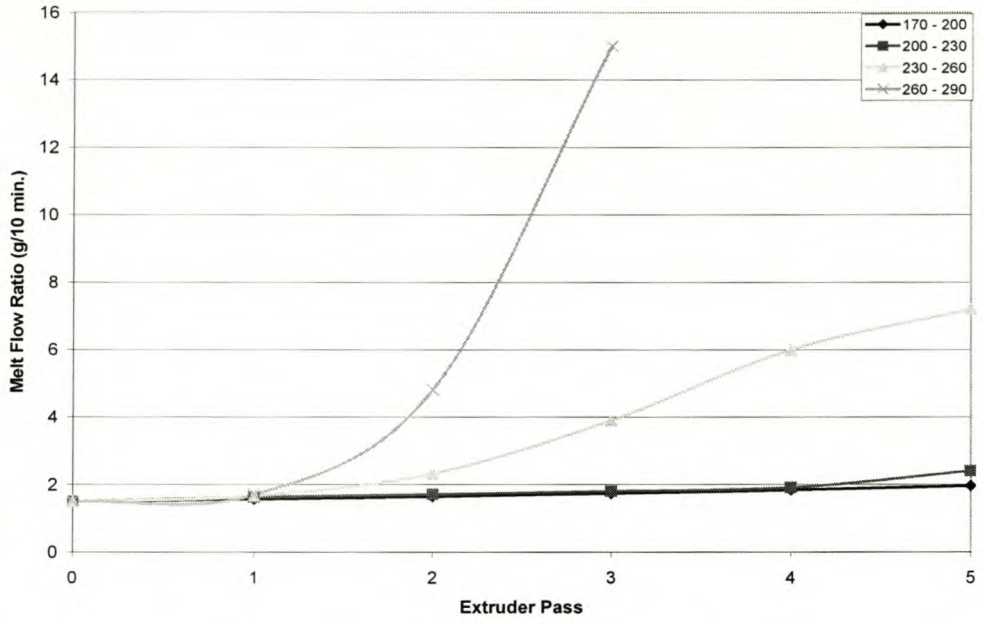

Figure 11.3: Degradation of an unstabilised propylene / 1-pentene copolymer at different processing temperatures.

11.2.2.3 Determination of Oxidation Induction Time (OIT)

The effectiveness of an antioxidant system in processing stabilisation is best assessed by multiple extrusion [11]. However, this is a very laborious and time-consuming exercise. Determination of thermo-oxidative stability by the determination of OIT is quick and relatively easy.

Thermogravimetric analysis [12] and DSC thermo-analysis [13] of propylene / 1-pentene random copolymers under dynamic inert conditions showed similar behaviour to the PP homopolymer. A stable melt region under inert conditions was found below a maximum melt temperature of 350 °C. Therefore a classical stabilisation package for propylene was used for all application studies.

Thermogravimetric determination of oxidation induction time (a criterion of stabilisation) and DSC determination of isotropic melt temperature (IMT) were conducted for a set of 8 propylene / 1-pentene random copolymer samples with different 1-pentene contents and compared with three PP homopolymer and four propylene / ethylene random copolymer samples. A description of the samples used in the stabilisation study can be found in Table 11.1. Results of oxidation induction time and isotropic melt temperature determinations are given in Table 11.2.

From the oxidation induction time measured at 120K/min all samples were considered to be stable for a minimum period of 30 minutes at 200°C. This temperature is well above the isotropic melt temperature defined as the temperature at which the last crystallite melts.

Table 11.2: Polymer thermal stability properties

Sample	Comonomer	Content (%)	OIT (sec)	IMT (°C)	MFI
1	No	0	358	180	40 *
2	No	0	589	180	2
3	Ethylene	3.0	287	180	2
4	Ethylene	3.0	413	175	12
5	No	0	391	180	1.4
6	Ethylene	2.1	253	175	8
7	Ethylene	2.8	758	170	3.2
8	1-pentene	1.5	425	170	1.5
9	1-pentene	1.5	190	175	7.5
10	1-pentene	1.5	524	175	12.5
11	1-pentene	3.5	227	170	1.5
12	1-pentene	3.5	335	170	1.5
13	1-pentene	3.5	837	170	12.5
14	1-pentene	3.5	229	170	45
15	1-pentene	3.5	250	165	1.5

* Premature degradation due to low Mw (shorter chains)

11.3 NUCLEATION

11.3.1 Introduction

Nucleating agents alter the crystalline structure of PP products by facilitating nucleation phenomena and thereby affecting the physical and/or optical property [1]. Among the wide range of nucleating agents used in industrial products the most important are mineral (talc) or organic nucleating agents [2]. The latter class is superior in providing PP products with enhanced clarity and is thus called “clarifiers”. As mentioned in paragraph 11.1 can the organic clarifiers be broken down into two classifications, namely:

- Melt sensitive
- Melt insensitive

Particularly active melt insensitive clarifiers are alkali metals or aluminium salts of aromatic or alicyclic carboxylics, e.g. sodium benzoate. However, melt sensitive clarifiers, typically derivatives of sorbitol, in comparison to all other available nucleating agents, provide PP with enhanced clarity and as such were used in this study.

An investigation of the nucleation behaviour of nucleated propylene / 1-pentene random copolymer properties was carried out by Milliken Chemical. Non-stabilised reactor grades were stabilised and nucleated with Millad 3988 and presented excellent haze performance and improved nucleation performance. Table11.3 presents haze values and shows the change in crystallisation peaks for the samples containing 3,5 and 5,5 % 1-pentene. The depression of the peak crystallisation temperature corresponds with increasing monomer content.

Table 11.3 Nucleated propylene/1-pentene copolymer properties

Sample	1-pentene content	Millad 3988 (ppm)	Crystallisation peak °C	Haze (%)
12	3,5	0	94,1	48,2
12	3,5	1500	106,9	16,2
12	3,5	2500	109,6	8,6
15	5,5	0	89,7	70,1
15	5,5	1500	107,2	12,0
15	5,5	2500	109,5	7,5

11.4 APPLICATION STUDY

11.4.1 Blow moulding

11.4.1.1 Blow moulding evaluations on PP polymers

A range of PP copolymers was evaluated for their suitability for processing by blow moulding. The essential properties of the blow-moulded articles are tabulated below in Table 11.4.

A Fischer single station blow-moulding machine, equipped with a modified, general-purpose screw was used. The screw configuration was characterised by a 1:1,8-compression ratio and a length-to-diameter (LD) ratio of 18,5. Temperature profiles were selected to give a final (parison) melt temperature of 205°C and the mould temperature was 12°C. The die had an outside diameter of 19,87 mm and an inside diameter of 15,5 mm. The article had a maximum diameter of 70 mm. The effective blow ratio of the article varied from 1,4 to 3,5.

Impact strength was determined by filling the containers with water and dropping them from increasing heights. Containers rated 5 survived a 3-meter drop height without failing. All other impact strength results were graded accordingly. The base weld was evaluated on the basis of the amount of material forming the weld. In all instances the weld was complete and was formed by at least 100% of the wall thickness. From the impact results there were no failures on the weld line or in close proximity. It was found however that the temperature should be kept about 10°C lower than the temperatures used for PP homopolymers and copolymers with similar MFR's in order to obtain a comparable base wield integrity.

The surface finish for all specimens tended to show die lines quite clearly. In addition there was some evidence of melt fracture on the surfaces. Only specimen 15 had a smooth fracture-fee surface. Specimen 5 had the worst fracture surface, with some transverse flow lines.

Table 11. 4 Essential properties, and article weights, of the blow moulded articles made from a range of PP copolymers

	# 12 - 3,5% C5, nucleated	# 5 - PP homo-polymer, Nucleated	# 7 - 2,8% C2, nucleated	# 8 - 1,2% C5, non-nucleated	# 11- 3,5% C5, non-nucleated	# 15 - 5,5% C5, nucleated
Article weights	19,70	17,16	19,80	20,90	20,03	20,05
Die swell	1.14	1.01	1.14	1.2	1.1	1.1
Impact strength	3	2	4	2	5	5
Clarity	4 y	2	3	2	3	4
Base weld	4	3	4	3	3	3
Die lines/ Surfaces	3 1 + f	2 f	3 1 + f	3 1 + p	3 1 + f	4 -
Thickness distribution	4	4	4	4	4	4
Gloss and surface Appearance	4	2	3	3	3	5

Ratings: 5: excellent, 4: good, 3: acceptable, 2: poor, 1 unacceptable
Additional symbols- y: yellowness, l: lines, f: surface fracture, p: pitting

Gloss and surface appearance of the propylene / 1-pentene random copolymers were superior to PP homopolymer and ethylene random copolymers. The shape of the moulded container was such that there could be a gradual grading of thickness of the container wall. In all cases there were no disparities or thickened regions of the wall. The nucleated 1-pentene random copolymers exhibited the best clarity.

Nucleated sample 8 and non-nucleated samples 11 and 15, described in Table 11.1, were selected for melt strength trials. Melt strength determination was performed courtesy of Borealis AG-Austria and the results presented in Table 11.5 below. Measurements of melt strength and melt drawability showed that propylene / 1-pentene copolymers were comparable with the PP homopolymer.

Table 11.5 Melt strength and melt drawability properties of some copolymer melts

Sample	Melt strength (cN)	Melt drawability (mm/sec)
8	125	15,8
11	122	14,1
15	121	15,5

11.4.1.2 Conclusions

It was possible to produce blow-moulded products with all the above materials. These materials are remarkable in their tolerance for a wide range of processing conditions. Temperature and shear conditions were varied by a few degrees and this had no marked effect on the product.

The processing performance and product performance of propylene / 1-pentene random copolymer samples 11, 12 and 15 were superior to the rest of the samples evaluated. The clarity of samples 12 and 15 were the best of the group.

11.4.2 Biaxially Orientated PP (BOPP) Film

11.4.2.1 Introduction

The results of the thermal and rheological characterisation study conducted on the family of propylene / 1-pentene random copolymers encouraged the idea to determine the behaviour of these random copolymers in biaxial orientation processes. Trial runs were conducted courtesy Bruckner, Germany, one of the world largest producers of equipment dedicated to bi-orientation of polymers.

The mechanical, optical and shrinkage properties of biaxially orientated film produced from a range of propylene / 1-pentene random copolymers, at different stretch ratios, were determined. The materials used in the study are listed below.

Table 11.6: Materials used in BOPP trial runs

Material	1-Pentene Content	MFR	Nucleated
Sample A	1.5%	1.5	Yes
Sample B	5%	1.5	Yes
Sample C	3%	1.5	Yes
Sample D	3%	1.5	No

11.4.2.2 Results and discussion

The full set of results is presented in Tables 11.7(a) and 11.7(b). Film was successfully produced from material A at a stretch ratio of 8x8 and a temperature of 143°C. At higher temperature (147°C) a 9x9 stretch ratio was possible. Film produced from material A characterises a grade with high stiffness and very good optical properties.

The optimum processing conditions for material D were found at a temperature of 135°C and stretch ratio of 8x8. Film produced from material D also exhibited high stiffness and good optical properties. Material D was then nucleated with Millad 3988 at a typical loading level of 2200 ppm and is presented as material C. Comparing the optical, mechanical and shrinkage properties of film produced from material C to film produced from material D, at identical processing conditions, it is

TABLE 11.7(a) : RESULTS FROM BOPP FILM TRIALS

Sample				A 9x9 147°C		B 8x8 129°C		B 8x8 135°C		B 10x10 135°C		
No	Description		Unit	Average	St.Dev.	Average	St.Dev.	Average	St.Dev.	Average	St.Dev.	Method
1	Thickness	-TD	µm	**10**	1.22	**12.14**	0.65	**9.57**	0.88	**6.02**	0.65	DIN 53370
2	Tensile	-MD	N/mm²	**199**	8.1	**188**	5.5	**146**	5.8	**157**	13	ASTM D 882
	Strength	-TD	N/mm²	**213**	11	**194**	6.9	**156**	9.9	**163**	6.4	ASTM D 882
3	Elongation	-MD	%	**64**	8.3	**64**	4.1	**90**	10	**46**	7.9	ASTM D 882
	At Break	-TD	%	**73**	8.6	**73**	4.3	**81**	9.1	**79**	5.6	ASTM D 882
4	Modulus of	-MD	N/mm²	**2931**	134	**1703**	54	**1514**	54	**1938**	145	ASTM D 882
	Elasticity	-TD	N/mm²	**2936**	126	**1685**	39	**1592**	110	**1647**	43	ASTM D 882
5	Coefficient			**ND**	ND	**ND**	ND	**ND**	ND	**ND**	ND	ND
	of Friction			**ND**	ND	**ND**	ND	**ND**	ND	**ND**	ND	ND
6	Haze		%	**0.7**	0.1	**0.5**	0.1	**0.7**	0.1	**0.4**	0.04	ASTM 1003
7	Gloss		-	**95**	1.6	**96**	2	**96**	0.8	**95**	2.6	ASTM 2457
8	Thermal 120/5	-MD	%	**5.8**	0.29	**23.3**	0.58	**11.5**	0.5	**14.1**	0.63	BMS TT 02
	Shrinkage 120/5	-TD	%	**5.4**	0.25	**22.9**	0.75	**11.5**	0.5	**14.3**	0.96	BMS TT 02
9	Thermal 130/5	-MD	%	**8.6**	0.63	**40.3**	1.53	**21.3**	1.15	**23.5**	2.04	BMS TT 02
	Shrinkage 130/5	-TD	%	**8.3**	0.65	**38.2**	0.76	**21.3**	1.15	**23.9**	1.31	BMS TT 02

TABLE 11.7(b) : RESULTS FROM BOPP FILM TRIALS (CONTINUED)

Sample				D 8x8 135°C		C 8x8 135°C		A 8x8 143°C		
No	Description		Unit	Average	St.Dev.	Average	St.Dev.	Average	St.Dev.	Method
1	Thickness	-TD	µm	**11.92**	0.67	**12.61**	0.6	**12.54**	1.12	DIN 53370
2	Tensile	-MD	N/mm²	**219**	15	**230**	8.6	**258**	11	ASTM D 882
	Strength	-TD	N/mm²	**206**	7.6	**234**	8.2	**267**	18	ASTM D 882
3	Elongation	-MD	%	**79**	9	**77**	4.4	**84**	6.8	ASTM D 882
	At Break	-TD	%	**81**	9.8	**94**	6.5	**83**	3	ASTM D 882
4	Modulus of	-MD	N/mm²	**2098**	39	**2116**	69	**2605**	28	ASTM D 882
	Elasticity	-TD	N/mm²	**1996**	37	**1985**	28	**2736**	158	ASTM D 882
5	Coefficient			**ND**	ND	**ND**	ND	**ND**	ND	ND
	of Friction			**ND**	ND	**ND**	ND	**ND**	ND	ND
6	Haze		%	**0.6**	0.1	**0.5**	0.1	**0.4**	0.1	ASTM 1003
7	Gloss		-	**96**	0.8	**96**	0.4	**98**	1.4	ASTM 2457
8	Thermal 120/5	-MD	%	**12.8**	0.29	**12.8**	0.29	**10.5**	2.6	BMS TT 02
	Shrinkage 120/5	-TD	%	**13.2**	0.76	**13.3**	0.58	**8.5**	0.5	BMS TT 02
9	Thermal 130/5	-MD	%	**22.3**	0.76	**23**	1	**13.7**	0.58	BMS TT 02
	Shrinkage 130/5	-TD	%	**22.7**	2.02	**23**	1.73	**14**	1	BMS TT 02

evident that nucleation has minimum effect on the properties and does not justify the additional expense of nucleation.

Optimising the processing conditions for material B the best results were obtained at a processing temperature of 135°C and a stretching ratio of 10x10. Comparative results are also presented for a stretching ratio of 8x8 at processing temperatures of 129°C and 135°C respectively.

No clear relationship between comonomer content and optical properties (haze and gloss) could be established. However, an indirect relationship between stiffness and comonomer content was evident. A slight improvement in both the optical and stiffness properties were obtained through nucleation and the use of higher stretch ratios. Optimum stretching temperature range for random copolymers with 1,5% 1-pentene content was 145-150°C, for 3% content 135-145°C and for 5% content 125-135°C. The film thickness is a function of the stretch ratio with a film thickness of less than 6 micron being obtained at a stretch ratio of 10x10. Outside the scope of this experiment a stretch ration higher than 10x10 was applied to obtain a film of 1 micron.

11.4.2.3 Conclusion

The combination of processability and premium film properties presents a unique opportunity for the family of propylene / 1-pentene random copolymers in BOPP applications. Material A with a 1-pentene content of 1.5% gave a film with the best balance of properties.

11.4.3 Cast film applications

11.4.3.1 Experimental

In a preliminary study cast films produced from propylene / 1-pentene random copolymer samples 8 and 11, with 1.2 wt% and 3.8 wt% comonomer content respectively, were compared to film produced from sample 3, a propylene / ethylene random copolymer with 3 wt% comonomer content. Both samples 3 and 8 were nucleated. A Fourie-Bonn extruder equipped with a 30mm screw, operated at 60 rpm, with a temperature profile setting as shown in Table 11.8, was used to produce cast film 50 µm thickness.

Table 11.8: Film extruder temperature settings

Zone	Temperature (°C)
Zone 1	195
Zone 2	205
Zone 3	215
Zone 4	230
Zone 5	235
Melt	240
Die	240

11.4.3.2 Results and discussion

The films were characterised with regard to their mechanical and optical properties and the results tabulated below.

Table 11.9: Properties of cast film

Sample	Yield strength (Mpa)[1]		Break strength (Mpa)[1]		Tear strength (g/µm)[2]		Haze (%)[3]	Gloss (%)[3]
	MD	TD	MD	TD	MD	TD	(%)	(U)
3	35.0	32.0	32.3	32.2	0.71	1.41	16,7	38
8	35.7	32.7	382	35.7	0.61	0.73	6,0	50
11	32.8	30.3	47.5	33.3	0.58	2.30	29,0	16

1 ASTMD 882
2 ASTMD1922
3 ASTMD1003/2457

The 1-pentene random copolymer has much better optical properties compared to the ethylene random copolymer and similar mechanical strength.

11.4.3.3 Comparison of grades produced on commercial plant

To confirm the exciting results obtained with random copolymers produced on BASF's pilot plant and film produced on Fourie-Bonn laboratory cast line, a propylene / 1-pentene random copolymer produced on Sasol's Novolen plant was sent to BASF, Germany for evaluation. Cast film produced from the 1-pentene random copolymer was characterised and compared to a commercially available ethylene random copolymer with similar comonomer content (on a wt% basis) and peak melting point. The full set of results for the respective cast films, both with a thickness of 50 µm, is given in Table 11.10 below.

The propylene / 1-pentene random copolymer produced a superior film compared to the ethylene random copolymer especially with regard to the following properties:

- Low Xylene Soluble (XL) content
- Low haze value
- Reduced blocking tendency
- Improved stiffness
- Improved Dart-Drop impact test

However, the 1-pentene random copolymer film exhibited a higher overall nib-level that could be related to unstable reactor conditions during the production run. Although the sealing properties of the 3 wt% 1-pentene copolymer are similar to that of the 3 wt% ethylene copolymer, a 5 wt% 1-pentene copolymer film should give a (lower) seal initiation temperature (SIT) not easily obtainable with ethylene random copolymers.

Table 11.10: Comparison propylene / 1-pentene and propylene / ethylene random copolymer cast film properties

Property	Unit	Novolen 3225 MC	Polifin 5 MD 001
MFR	**G/10min**	7,4	7,9
Xylene solubles	%	4,8	1,4
DSC	°C	148,7	148,7
Melt enthalpie	J/g	83,9	90,9
Dynamic Crystallization	°C	100	108,3
Cast film			
Film quality	mark	4,5	5
Nib count			
>34µm	nibs/m²	1271	1701
-70µm	nibs/m²	1022	3121
-100µm	nibs/m²	219	2086
-150µm	nibs/m²	134	1624
-200µm	nibs/m²	59	672
-300µm	nibs/m²	28	485
-500µm	nibs/m²	9	204
-800µm	nibs/m²	3	56
-1500µm	nibs/m²	1	8
>1500µm	nibs/m²	0	0
total	**nibs/m²**	**2746**	**9956**
Cast film (50µm)			
Nib level	mark	4	4
Structure	mark	2	1,5
Stripes	mark	1,5	1,5
Haze Valnes			
BASF- Method	%	7,4	5,4
ASTM – Method	%	1,7	1,2
Gloss (20°)	%	115	117
Blocking force (70°C)	N	46	23
Coeffisient of friction		0,19	0,41
Dart-drop impact	G	432	474
Flexural modulus			
MD	N/mm²	481	571
TD	N/mm²	481	586

11.4.4 Blown film

Two propylene / 1-pentene random copolymer grades produced on the pilot plant, namely samples 8 (nucleated) and 11 (non-nucleated), was compared to Targor's Novolen grades 3200 H (non-nucleated) and 3240 H. The intention was to obtain blown film with similar transparency and mechanical properties as for the cast film. This was a high target, not reached with air-cooled PP blown film to date.

Extrusion conditions and test results obtained from the comparative study on the film produced are shown in Table 11.11 below. The results obtained from the cast film comparative study are confirmed by these results. The propylene / 1-pentene random copolymer films have a much better transparency in comparison to the ethylene randoms, both in the nucleated or non-nucleated state. In addition the gloss values for the 1-pentene randoms are much better than those measured for the ethylene random copolymers.

Table 11.11: Extrusion conditions and test results for blown film trial

	Unit	Novolen		Pentene	
		3200 H 2.8% C2, not nucleated	3240 H 3% C2, nucleated	PP B 2118 1,2% C5, nucleated	PP B 2119 3.8% C5, not nucleated
Reifenhauser 45 Extruder					
Throughput	Kg/h	30	30	30	30
Screw speed	Rpm	65	63	57	56
Melt temp.	°C	206	206	203	207
Blow ratio		1:2	1:2	1:2	1:2
Film thickness	µm	50	50	50	50
Film width	mm	471	471	471	471
Blown film					
Nib level	Mark	3	3	4	3,5
Haze	%	48,7	53,9	40,4	37,6
Haze	%	29,3	14,6	**3,5**	20,5
Gloss (20°)	%	16	23	58	17

The mechanical properties of the air-cooled blown film, shown in Table 11.12, are inferior compared to those films produced by cast or water quenched blown processes especially the tear (propagation) strength. This can be rationalised by the slow effective cooling rate of air-cooled blown process, compared to the other two processes, resulting in a higher degree of crystallisation.

Table 11.12: Mechanical properties of blown films

Batch #	Yield strength (Mpa) ASTM D 882		Break strength (MPa) ASTM D 882		Elongation (%) ASTM D 882		Tear strength (g/µm) ASTM D 1922		Modulus (MPa)	
	MD	TD	MD	TD	MD	TD	MD	TD	MD	TD
8	35.70	32.71	38.28	35.75	5	5	0.61	0.73	1095.9	1002.7
11	32.80	30.38	47.53	33.34	293	328	0.58	2.30	1129.3	867.0
3200H	31.87	30.55	47.06	36.84	297	349	0.09	1.60	857.7	852.0
3240H	35.06	32.07	32.35	32.26	254	7	0.71	1.41	963.9	937.7

11.4.5 Industrial film trials

For the field trials sample 8 was selected for the trial run on the water quenched blown film process at Safepack and sample 9 for the trial run on the cast film line at Multifoil. For the cast film trial run the propylene / 1-pentene random copolymer was compared to a 1.5 wt% ethylene random copolymer with similar MFR. The results from the film characterisation are pesented in Table 11.13.

Table 11.13: Comparison of films produced by different processes

Sample	Yield strength (Mpa)[1]		Break strength (Mpa)[1]		Tear strength (g/µm)[2]		Haze (%)[3]	Gloss (%)[3]
	MD	TD	MD	TD	MD	TD	(%)	(U)
Cast	21.8	22.4	38.7	33.0	1.5	2.4	2.4	93
Blown	21.0	21.9	38.4	33.2	1.6	3.1	2.7	89
C3/C2	22.7	22.6	49.7	31.6	1.6	-	4.1	55

1 ASTMD 882
2 ASTMD1922
3 ASTMD1003/2457

Very good correlation between the cast film and water quenched blown film processes is obtained with regard to both the mechanical and optical properties of the propylene / 1-pentene random copolymer films. It is seen that the propylene/1-pentene film has better haze and gloss properties than the corresponding the propylene / ethylene random copolymer.

11.4.6 Injection moulding

A shrinkage study was performed on the set of samples as described in Table 11.1. In order to achieve an optimised melt temperature of 210°C at the extruder barrel exit temperature settings as described in Table 11.14 were used.

Table 11.14: Injection moulding barrel temperature settings

Zone	Temperature (°C)
Feed zone	40
Zone 1	190
Zone 2	200
Zone 3	210
Nozzle	210

Using different mould temperatures, shrinkage was calculated. Measurements were taken and replicas of the samples were aged for 16h. Total shrinkage as well as shrinkage during manufacture was determined. Figures 11.4 and 11.5 show the results for mould temperatures of 15 and 55°C respectively. The propylene / 1-pentene random copolymers present lower in-mould as well as total shrinkage than propylene homopolymers and ethylene random copolymers.

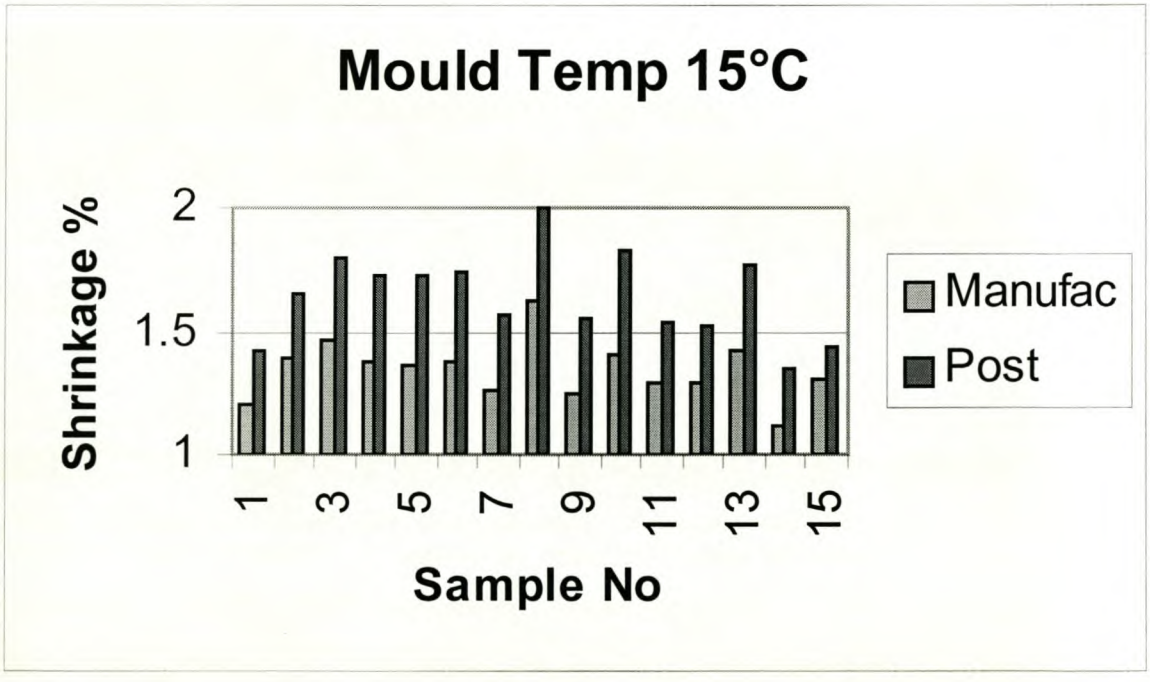

Figure 11.4: Mould shrinkage at 15°C

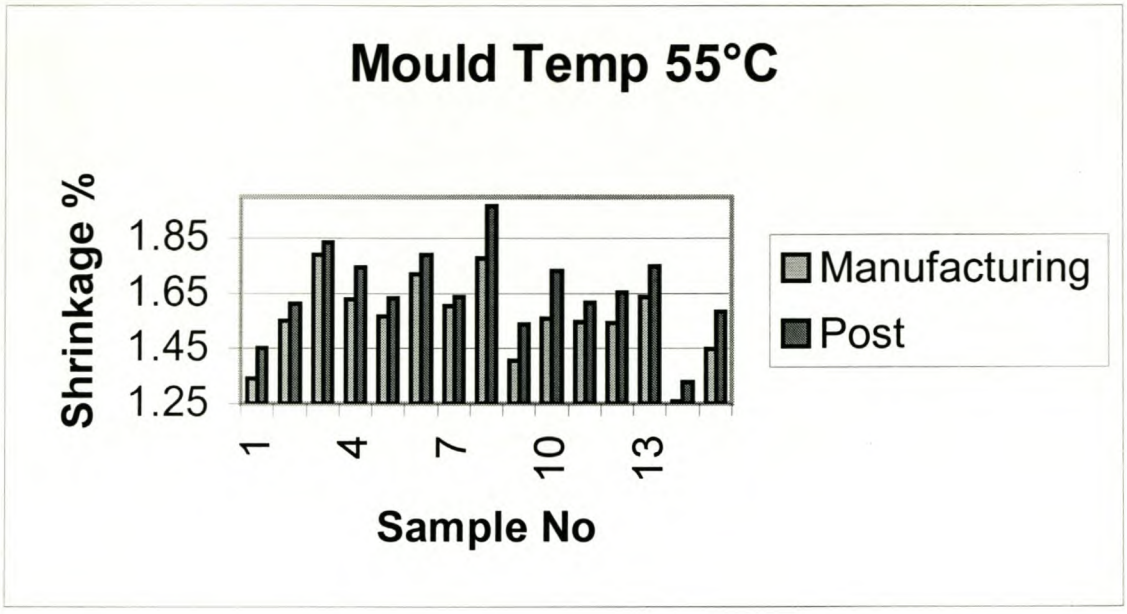

Figure 11.5: Mould shrinkage at 55 °C

Samples 10, 13 and 14 (see Table 11.1) were selected for injection moulding field trials. All 3 switch-over methods: time, stroke and internal pressure were investigated. It was found that by using any of the methods, articles of consistent quality could be produced. As the heat stability of the samples was found to be good, a long dwell time in the barrel did not create any problems. For a screw diameter of 32mm a screw speed of 40 rpm was found to be optimal. The optimum shot size was found to be below 4D, where D is the diameter of the screw. A feed zone temperature of 35 – 40˚C is recommended for all samples. The barrel temperature should be selected to achieve an optimum melt temperature of 210ºC. The propylene / 1-pentene random copolymers are suitable for injection moulding on equipment currently used for PP processing with no special plasticising units and using similar injection velocities and pressures.

11.5 CONCLUSIONS

The degree of crystallinity of the propylene / 1-pentene random copolymers is a primary contributor to the excellent application properties of this new family of random polypropylenes. On the other hand, susceptibility to thermo-oxidative degradation is increased. Due to the lowering of the melting and subsequently the processing temperatures with increased 1-pentene content this effect is practically cancelled.

Propylene / 1-pentene random copolymers have good balance of qualities to make them very useful in the market. Apart from well-balanced tensile properties and good impact strength they have excellent optical properties and very low soluble content.

The injection moulding and blow moulding market can expect to profit from these excellent copolymers. We expect the propylene/1-pentene random copolymers to dominate in the high clarity film market. Other applications such as oriented film, thermoforming and sealing layers also offer potential applications.

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CHAPTER 12

CONCLUSIONS

Polypropylene's extreme versatility makes it the polymer today with the greatest potential for replacing other materials such as PVC, PET and polystyrene. It uses the petrochemical by-product propylene as feedstock material that should remain cheaper than ethylene and has a clean image with environmentalists. The innovative potential of PP is far from exhausted, and the importance of soft, flexible grades will increase significantly, creating even more opportunities. There is hardly any other thermoplastic that is so economical to use and, at the same time, universally applicable.

Most polypropylene copolymers commercially available have ethylene, and to a lesser degree 1-butene as comonomers. Available higher α-olefins, mostly even-numbered, are seldom used for the production of copolymers, probably due to cost. Sasol's Fischer-Tropsch oil-from-coal process produces many linear and branched α-olefins as by-products that can be isolated and purified by a relatively cheap refinery process, including the odd-numbered 1-pentene olefin. Sasol's gas-phase Novolen PP plant at Secunda, South Africa, is ideally suited to the manufacture of high quality PP random copolymers. As such an opportunity was identified to research the use of higher α-olefins, and more specifically 1-pentene, in the gas-phase production of PP random copolymers.

A procedure was developed to produce propylene / 1-pentene random copolymers in the gas-phase in 10 litre autoclaves. It was found that commercially available fourth generation supported catalysts successfully incorporated the bulky 1-pentene monomer into the propylene backbone. Through software modelling, supported by experimental data from laboratory copolymerisation reactions, it was proven that typical process conditions could be employed during the gas-phase polymerisation of propylene and 1-pentene without the risk of condensation taking place inside the reactor.

Propylene / 1-pentene random copolymers were subsequently successfully produced on the 800 litre BASF pilot plant in Germany followed by the first commercial production of the copolymer on Sasol's 50m^3 Novolen gas-phase plant at Secunda. Using commercially available software the impact of introducing 1-pentene as comonomer during the production of random copolymers on the condenser cooling capacity was evaluated. The results obtained showed a 20% increase in cooling capacity. Feasible and safe plant operating conditions were established for the production of propylene / 1-pentene random copolymers.

It was proven that propylene / 1-pentene random copolymers could be produced at higher pressure in the commercial plant compared to feasible process conditions using ethylene as comonomer. Operating at higher pressure increases the monomer concentration in the reactor and as such improves the space/time/yield ratio of the 50m^3 reactors. An increase in catalyst productivity was also observed up to a comonomer ratio of about 5%.

The relevant analytical techniques were developed to enable both molecular and macroscopic characterisation of propylene / 1-pentene random copolymers. This was followed by a comprehensive study to compare the rheological, thermal, physical and mechanical properties of propylene / 1-pentene random copolymers with those of commercially available PP random copolymers.

The propylene / 1-pentene random copolymers show unique rheological behaviour associated with the short propyl branches in the polymer backbone. The 1-pentene random copolymers have good processability with rheological properties similar to PP homopolymer. The viscosity of the 1-pentene copolymer shows higher shear and temperature sensitivity compared to propylene homo- and ethylene random copolymers.

It was proposed that the short branch "defects" in the polymer backbone are incorporated into the crystal lattice resulting in increased rate of melting point depression with increasing (wt%) comonomer content compared to other random copolymers while maintaining relative high stiffness. The propylene / 1-pentene random copolymers exhibit the lowest haze values compared to all commercially available PP random copolymers at corresponding levels of comonomer content on a wt% basis. The stiffness to haze ratio of propylene / 1-pentene random copolymers are unique for all the members of the PP family.

Application studies conducted on the propylene / 1-pentene random copolymers highlighted several interesting characteristics. Films produced from these copolymers exhibited very low haze and xylene soluble values while maintaining mechanical integrity. In the BOPP application the combination of processability and premium film properties presents a unique opportunity for the family of propylene / 1-pentene random copolymers.

Blow moulding and injection moulding trials highlighted several advantages of product properties manufactured with propylene / 1-pentene random copolymers if compared to other commercially available random copolymers. The 1-pentene randoms presented lower in-mould as well as total shrinkage than ethylene based random copolymers.

Stabilisation and nucleation studies conducted on the propylene / 1-pentene random copolymers showed that a typical combination antioxidant package and nucleating agent, at normal loading levels, could be used.

In the larger PP random copolymer family 1-pentene imparts a better balance of properties than other comonomers. The combination of low melting point and xylene solubles with high stiffness and clarity is unique to propylene / 1-pentene random copolymers.

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